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Organic Chemistry.

Superheating of Uniform Organic Compounds. I. Aryl-paraffins and Aliphatic Esters. S. Skraup and F. Nieten.—(See i, 1185.)

Condensation of Acetylene with Hydrogen Sulphide in Presence of Aluminium Oxide. A. E. Tschitschibabin and O. S. Bagdassarjanz (*J. pr. Chem.*, 1924, [ii], **108**, 200—208).—When acetylene (2 vols.) and hydrogen sulphide (1 vol.) are passed over aluminium oxide at 425—450°, a liquid product is obtained, consisting of thiophen (40%), 2- and 3-ethylthiophen, mercaptans, unsaturated hydrocarbons, and products of b. p. above 186°. The catalyst loses its activity rapidly; the specific gravity of the crude condensation product decreases as the catalyst ages. (Cf. Tschitschibabin, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 709.)

F. G. W.

Action of Alkali on Ethyl Alcohol and the "Nitric Oxide Reaction" of W. Traube. M. Stechow (*Ber.*, 1924, **57**, [*B*], 1611—1615).—Contrary to previous assumptions, the action of nitric oxide on an alcoholic solution of sodium ethoxide or hydroxide leads invariably to the production of considerable amounts of the compound, $CH_2[N(NO)\cdot ONa]_2$, identical with the product isolated by Traube by the action of nitric oxide on a solution of acetone in alcohol in the presence of alkali. The production of the salt depends entirely on the quantity of alkali present and the duration of the experiment; it ceases with exhaustion of the alkali, but starts again after addition of further amounts of the latter. The source of the product is unknown, but it is significant that the protracted action of alkali ethoxide or hydroxide on ethyl alcohol in the absence of oxygen leads to the formation of resin acids, acetaldehyde, acetic acid, and condensation products of acetone such as mesityl oxide, phorone, and mesitylene. Traube's reaction is therefore unsuitable for the elucidation of constitutional problems.

H. W.

Vapour-pressure Curves for Systems containing Alcohol, Ether, and Water. E. A. Louder, T. R. Briggs, and A. W. Browne (*Ind. Eng. Chem.*, 1924, **16**, 932—935).—By the static method (the apparatus is described and figured), the vapour pressures of ethyl alcohol and of ethyl ether have been determined for the temperature range 0—50°. The values obtained are generally a little higher (about 0·5 mm. for ether, 0·5—1 mm. for alcohol) than those of Ramsay and Young or of Regnault. The vapour pressures of mixtures of (i) alcohol and ether, (ii) alcohol, ether, and water, and (iii) alcohol (95%), ether, and diphenylamine, were also measured over the same temperature range.

W. A. S.

Pyrogenic Decomposition of Propyl Alcohol. (MLLE.) E. PEYTRAL (*Bull. Soc. chim.*, 1924, [iv], **35**, 960—964; cf. A., 1920, i, 217).—By the methods previously employed (A., 1918, i, 1), it is shown that propyl alcohol when passed through a platinum tube at high temperatures undergoes the two primary decompositions: $CH_2Et{\cdot}OH=Et{\cdot}CHO+H_2$ and $CH_2Et{\cdot}OH=CHMe{:}CH_2+H_2O$, the former reaction, which requires the least deformation of the molecule, slightly preponderating. The propaldehyde undergoes further decomposition to give ethane and carbon monoxide, whilst the ethane is partly decomposed to ethylene and hydrogen. A small quantity of acetylene is also formed, probably by decomposition of ethylene, and traces of formaldehyde were detected, probably due to the primary decomposition: $CH_2Et{\cdot}OH=H{\cdot}CHO+C_2H_6$. R. B.

Components of Wood Spirit Oil. II. H. PRINGSHEIM and A. GORGAS (*Ber.*, 1924, **57**, [*B*], 1561—1566; cf. A., 1923, i, 1052).—The portion of the oil, b. p. 90—130°, which is not attacked by sodium hydrogen sulphite has been separated into four components: (1) Δ^{α}-buten-γ-ol, b. p. 97°, characterised by oxidation to pyruvic acid and by reduction to *sec.*-butyl alcohol; (2) diethyl ketone; (3) 2 : 5-dimethyltetrahydrofuran, b. p. 108°, characterised as the ferrocyanide, and (4) 2-methyl-5-ethyl-4 : 5-dihydrofuran, m. p. 125°, which is converted by warm water into ethyl γ-hydroxy-*n*-butyl ketone. A method is given for the determination of methyl propyl ketone and diethyl ketone in mixtures which depends on the difference between their velocities of oximation. H. W.

Dilution of Ethylene Bromohydrin with Water. J. READ and G. J. BURROWS (*J. Proc. Roy. Soc. N.S. Wales*, 1923, **57**, 54—57; cf. T., 1920, **117**, 1214).—When water is added to ethylene bromohydrin, a negative thermal effect is produced up to a dilution of about 80% followed, at about 75%, by a positive thermal effect which persists to a dilution of about 10%. Conversely, on adding small amounts of ethylene bromohydrin to water the initial positive thermal effect is followed by a negative effect. The density–concentration curve is regular and of the same type as the refractive index–concentration curve (cf. *loc. cit.*). At 20°, a maximum contraction (1·07%) occurs at a concentration of about 50%, and at 25°, at a concentration of about 46% of ethylenebromohydrin. The viscosity of solutions increases regularly with an increasing proportion of the bromohydrin. W. T. K. B.

Pyrogenic Decomposition of Ethyl Ether. (MLLE.) E. PEYTRAL (*Bull. Soc. chim.*, 1924, [iv], **35**, 964—968).—When the vapour of ethyl ether is passed rapidly through a platinum tube at high temperatures, the only primary reaction is its decomposition into ethane and acetaldehyde. The latter substance undergoes secondary decomposition into carbon monoxide and methane as previously shown (A., 1920, i, 217), whilst the ethane partly decomposes into ethylene and hydrogen, a fraction of the ethylene undergoing a tertiary decomposition to acetylene and hydrogen when the

velocity of the gas through the tube is relatively low. Decomposition of the ether to give water and 2 mols. of ethylene or 1 mol. of *cyclo*butane either does not take place or occurs only to a negligible extent, the primary decomposition being thus that which involves the least deformation of the molecule. R. B.

Decomposition of Ethers by Metallic Sodium. II. Relative Tenacity of Different Radicals to the Oxygen Atom. P. SCHORIGIN.—(See i, 1185.)

Glyceryl Tri-*m*-nitrobenzoate. F. STATHER (*Ber.*, 1924, **57**, [*B*], 1392—1393).—*Glyceryl tri*-m-*nitrobenzoate*, m. p. 130° (corr.), is prepared by the action of *m*-nitrobenzoyl chloride on glycerol in the presence of chloroform and quinoline. The substance, m. p. 161°, described under this name by Bauer (this vol., i, 825) is probably *m*-nitrobenzoic anhydride. The interchange of acyl radicals during the acylation of mono- or di-glycerides in the presence of quinoline has not yet been observed. H. W.

Behaviour of Esters of Metaphosphoric Acid and of Phosphorous Acid towards Hydrazine, Hydroxylamine, and their Derivatives. W. STRECKER and H. HEUSER (*Ber.*, 1924, **57**, [*B*], 1364—1372).—The action of an excess of hydrazine hydrate causes hydrolysis of metaphosphoric esters. If, however, molar quantities of the reactants are brought together in chloroform solution, *ethyl hydrogen orthophosphorhydrazide*,

$$O{:}P(OH)(OEt)\cdot NH\cdot NH_2,$$

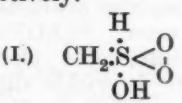
a viscous, multimolecular liquid, is produced. *Ethyl hydrogen orthophosphorphenylhydrazide*, m. p. 192°, and *ethyl hydrogen orthophosphor*-p-*tolylhydrazide*, m. p. 195°, are similarly produced. *p*-Bromophenylhydrazine forms the corresponding p-*bromophenylhydrazide*, m. p. 187°, with considerably greater difficulty, whereas *p*-nitrophenylhydrazine does not appear to react. Highly purified hydroxylamine and ethyl metaphosphate yield *ethyl hydrogen phosphorhydroxylamide*, $O{:}P(OH)(OEt)\cdot NH\cdot OH$, a syrupy liquid, but derivatives such as phenylhydroxylamine do not react.

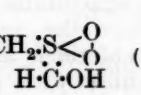
Ammonia does not react with triphenyl or tri-*p*-tolyl phosphite at the atmospheric temperature, whereas hydrolysis takes place under more energetic conditions. Similarly, hydrazine hydrate is inactive in the cold, but when warmed yields a mixture of hydrazine phenoxide or *p*-tolyloxide and *dihydrazine hydrogen phosphite*, $P(OH)_3,2N_2H_4,H_2O$, m. p. 105°. The use of halogenated phosphorous esters facilitates but does not alter the character of this reaction. Thus the monohalogenated ester, $PCl(OEt)_2$, gives ammonium chloride, ammonium phosphite, and phenol with ammonia, whilst with hydrazine hydrate it yields dihydrazine hydrogen phosphite, hydrazine phenoxide, and hydrazine hydrochloride. The dichloride, $PCl_2(OEt)$, gives the same products with greater readiness. Triethyl phosphite is not affected by hydrazine hydrate, possibly on account of its relatively low boiling point, whereas diethyl hydrogen phosphite gives dihydrazine hydrogen phosphite. The presence of a halogen atom attached to phosphorus facilitates the hydrolysis.

The normal esters of orthophosphoric or thiophosphoric acid do not react with hydrazine or ammonia. If, however, a halogen atom is present in place of an organic residue, it suffers replacement with production of the corresponding amide or hydrazide. The following new compounds are thus produced: p-*Tolylthiophosphordiamide*, $S{:}P(NH_2)_2{\cdot}O{\cdot}C_6H_4{\cdot}Me$, m. p. 84°; *phenylthiophosphordihydrazide*, $S{:}P(NH{\cdot}NH_2)_2{\cdot}O{\cdot}Ph$, m. p. 95°; p-*tolylthiophosphordihydrazide*, m. p. 106°; *phenylorthophosphordihydrazide*. H. W.

Sulphoxyl Compounds. XIII. Reduction of Aldehydesulphoxylates. A. Binz, C. Räth, and E. Walter (*Ber.*, 1924, **57**, [*B*], 1398—1403; cf. A., 1921, i, 30).—The oxidising action of aldehydesulphoxylates is illustrated by the production of the corresponding disulphides from formaldehydesulphoxylate and thiophenol or *o*-thiocresol, and from formaldehydesulphoxylate which has been condensed with *o*-anisidine or methylamine and thiophenol and ethyl mercaptan. Sodium formaldehydesulphoxylate is reduced by hypophosphorous acid or, in a more complex manner, by hydrogen sulphide to *bishydroxymethyl disulphide*, $OH{\cdot}CH_2{\cdot}S{\cdot}S{\cdot}CH_2{\cdot}OH$, m. p. 155°, the yields being poor. Better results are obtained when the sulphoxylate is previously condensed with a secondary amine; thus, formaldehydesulphoxylate, piperidine, and hypophosphorous acid or hydrogen sulphide give *dipiperidinomethyl disulphide*, $S_2(CH_2{\cdot}NC_5H_{10})_2$, m. p. 42° (*hydrochloride*, m. p. 176°). *Diphenylhydroxymethyl disulphide*, $S_2(CHPh{\cdot}OH)_2$, m. p. 65° (decomp.), from benzaldehyde sulphoxylate and hypophosphorous acid, is decomposed by cold sodium hydroxide into sodium disulphide and benzaldehyde and by boiling hydrochloric acid into benzaldehyde, hydrogen sulphide, and sulphur. *Dibenzylmethylaminomethyl disulphide*, $S_2(CH_2{\cdot}NMe{\cdot}CH_2Ph)_2$, a yellow liquid (*hydrochloride*, m. p. 135°), and *di-2-methylpiperidinomethyl disulphide*, a viscous liquid which gives a crystalline *hydrochloride*, are described.

The constitution, $HO{\cdot}CH_2{\cdot}O{\cdot}S{\cdot}OH$, does not adequately explain the reduction of formaldehydesulphoxylate or the apparently dibasic nature of the substance (cf. Forke, *Diss.*, Berlin, 1923). Formaldehydesulphoxylic acid and diformaldehydesulphoxylic acid (Binz, A., 1918, i, 4) more probably have the constitutions I and II, respectively.

(I.) 

 (II.)

H. W.

Complex Compounds of Lead Acetate [and Propionate] and the Corresponding Salts of the Metals of the Alkaline Earths. R. Weinland and E. Bauer (*Ber.*, 1924, **57**, [*B*], 1508—1514).—In a previous communication (Weinland and Stroh, A., 1922, i, 981), it has been shown that lead forms with acetic acid

residues polynuclear acetato cations. Salts are now described in which the lead atoms are partly replaced by other metallic atoms.

Lead sodium acetate nitrate, $[PbAc_2Na]NO_3,H_2O$, is prepared by the spontaneous evaporation of an aqueous solution of lead acetate and sodium nitrate. The following *salts* are prepared in a similar manner: (1) $[Pb_2(CH_3{\cdot}CH_2{\cdot}CO{\cdot}O)_4Na]ClO_4$;
(2) $[Pb(OAc)_2Sr](ClO_4)(OAc),4H_2O$;
(3) $[Pb_2(CH_3{\cdot}CH_2{\cdot}CO_2)_2(OH)_2Na](ClO_4)(C_3H_5O_2)$,
(4) $Pb(C_3H_5O_2)_2,Pb(OH)_2,NaC_3H_5O_2,NaClO_4$;
(5) $[Na_2(OAc)_2Ba](NO_3)_2,2H_2O$; (6) $[Ba(OAc)_2Mg](ClO_4)_2$. These are all colourless, well-crystallised compounds of which (2) and (6) can be recrystallised unchanged from water.

Calcium and strontium resemble lead in their ability to yield acetato cations, which is established by the isolation of the *salts*: $[Ca(OAc)_2Ca](ClO_4)_2,2H_2O$; $[Sr(OAc)_2Sr](ClO_4)(OAc),4H_2O$; $[Sr(OAc)Sr](NO_3)_2,3H_2O$.

Lead propionate has hitherto been described as non-crystalline. The isolation of a crystalline *salt* containing half a molecule of water of crystallisation causes it to be regarded as the propionate of a lead-propionato base, $[Pb(C_3H_5O_2)_2Pb]C_3H_5O_2,H_2O$. This hypothesis is supported by the isolation of the salts: $[Pb(C_3H_5O_2)_2Pb](ClO_4)_2,2H_2O$ and $[Pb(C_3H_5O_2)_2Pb](BrO_3)_2,4H_2O$. Attempts to obtain similar propionato compounds from the crystalline barium propionate were unsuccessful. H. W.

Pyrogenic Decomposition, at High Temperatures, of Acetic Anhydride. (MLLE.) E. PEYTRAL (*Bull. Soc. chim.*, 1924, [iv], **35**, 969—974; cf. A., 1922, i, 219).—The sudden decomposition of acetic anhydride when rapidly passed through a platinum tube at high temperatures yields as primary products keten and acetic acid, the decomposition involving the least deformation of the molecule. The keten undergoes secondary decomposition into ethylene and carbon monoxide, whilst the acetic acid by secondary decomposition gives methane and carbon dioxide. Small amounts of acetylene and hydrogen are formed, partly by decomposition of the ethylene, but also, especially as the velocity of flow of the acetic anhydride vapour diminishes, by primary decomposition. Hydrogen is also produced, when the velocity of flow is relatively low, by decomposition of the ethylene, giving free carbon or complex hydrocarbons. R. B.

Composition of Soja Bean Oil. E. S. WALLIS and G. H. BURROWS (*J. Amer. Chem. Soc.*, 1924, **46**, 1949—1953).—The fatty acids contained in soja bean oil have been determined by the method of Twitchell (cf. A., 1914, ii, 685; 1917, ii, 428) and the results compared with those obtained in a detailed analysis by Jamieson and Baughmann (cf. A., 1923, i, 281). The percentages of the saturated acids were: palmitic 10, (6·8); stearic 2, (4·4); arachidic 1, (0·7); myristic 0, (—); lignoceric, —, (0·1); the figures in brackets being those of the analytical method. The

difference in the distribution between palmitic and stearic acids in the two sets has not been explained. A. C.

Trichloroacrylic Acid and some of its Derivatives. III. Peroxide of Trichloroacrylic Acid. J. Böeseken and H. Gelissen (*Rec. trav. chim.*, 1924, **43**, [v], 266—268).—The *peroxide of trichloroacrylic acid*, $(CCl_2{:}CCl{\cdot}CO)_2O_2$, m. p. 49°, is prepared by the action of hydrogen peroxide and sodium hydroxide on trichloroacrylyl chloride. It is not hydrolysed by water, is sensitive to shock, is very volatile, and attacks the skin. J. K.

Preparation of Dehydracetic Acid from Acetoacetic Ester. F. Arndt and P. Nachtweg.—(See i, 1223.)

Ferric Oxalate and its Application to the Separation of Iron and Calcium. J. Barlot (*Bull. Soc. chim.*, 1924, [iv], **35**, 1026—1030).—Ferric oxalate is obtained as an apparently amorphous, greenish-yellow substance, $Fe_2(C_2O_4)_3,4H_2O$, by the slow evaporation of a solution of ferric hydroxide in saturated oxalic acid solution. Its solution in water is more stable than that in oxalic acid, from which ferrous oxalate slowly separates. It forms stable double salts with other oxalates, and it is proposed to separate iron and calcium by taking advantage of the fact that in the presence of ammonium oxalate and acetic acid, the double calcium ferric oxalate is quantitatively decomposed into soluble ferric ammonium oxalate and insoluble calcium oxalate.

S. K. T.

Action of Light on Solutions of Organic Compounds in Chloropicrin. A. Piutti (*Atti I. Congr. naz. Chim. pur. appl.*, 1923, 437—438; from *Chem. Zentr.*, 1924, i, 2514; cf. A., 1921, i, 298).—Chloropicrin acts as an oxidising, chlorinating, or nitrating agent, respectively, according to the compound with which it is exposed to light. With acetic acid, oxalic and chloroacetic acids are formed together with chlorine, hydrochloric acid, and nitrous acid. Similarly, with ethyl succinate, succinic acid; with methyl salicylate, methyl chlorosalicylate, oxalic acid, and ammonium tetroxalate; with toluene, benzoic acid, *o*-nitrotoluene, and oxalic acid, and with naphthalene, benzoic and phthalic acids are produced. G. W. R.

Configuration of αα′-Dibromo-dibasic Acids. III. The αα′-Dibromosuccinic Acids. H. R. Ing and W. H. Perkin, jun. (*J. Chem. Soc.*, 1924, **125**, 1814—1830).—Methyl and ethyl esters of *dl*-dibromosuccinic acid described by Pictet and by Michael, but not definitely characterised, have now been obtained in a pure state. Bromination of ethyl maleate gave *ethyl* dl-*dibromosuccinate*, b. p. 137—138°/11 mm. *Methyl* dl-*dibromosuccinate* has m. p. 43°. *Ethyl* meso*dibromosuccinate*, m. p. 58°, and *methyl* meso-*dibromosuccinate*, m. p. 65°, were obtained by bromination of the corresponding alkyl fumarates.

Condensation of methyl and ethyl *dl*-dibromosuccinates with the sodium derivative of the corresponding malonic esters gave a

yield of 80—90% of the respective *cyclo*propane esters, both of which on hydrolysis yielded dl-cyclo*propane*-1 : 2 : 2 : 3-*tetracarboxylic acid*, dihydrate, m. p. 100°; anhydrous, m. p. 198—200°. d-cyclo*Propane*-1 : 2 : 2 : 3-*tetracarboxylic acid*, m. p. 195—196° (decomp.), $[\alpha]_D^{18}$ +106·5° in water, was obtained by resolving the *dl* isomeride by fractional crystallisation of the brucine salt. The *brucine* salt, $C_7H_6O_8,4C_{23}H_{26}O_4N_2,2H_2O$, has $[\alpha]_D^{18}$ −43·01°. When heated at 200°, the *d* acid is converted into inactive *trans-cyclo*propane-1 : 2 : 3-tricarboxylic acid, m. p. 220°.

Condensation of methyl *meso*dibromosuccinate with methyl sodiomalonate gives methyl-α-carbomethoxytricarballylate, methyl *cyclo*propane-1 : 2 : 2 : 3-tetracarboxylate, and methyl ethanetetracarboxylate. By condensation of ethyl *dl*-dibromosuccinate and ethyl sodiocyanoacetate, a 90% yield of *ethyl* 2-*cyano*cyclo*propane*-1 : 2 : 3-*tricarboxylate*, b. p. 200—205°/8 mm., was obtained; this gave on hydrolysis *dl-cyclo*propanetetracarboxylic acid. The main product from ethyl *meso*dibromosuccinic acid and ethyl sodiocyanoacetate was methyl α-cyanotricarballylate.

Ethyl *dl*-dibromosuccinate reacts in the cold with ethyl sodiobenzoylacetate to give ethyl 5-phenyl-2 : 3-dihydrofuran-2 : 3 : 4-tricarboxylate, b. p. 227—230°/12 mm., which on hydrolysis yields *α-hydroxy-γ-benzoyltricarballylic acid*,

$$CO_2H\cdot CHBz\cdot CH(CO_2H)\cdot CH(OH)\cdot CO_2H,$$

m. p. 142—143° (decomp.); this acid, when heated above its melting point, is converted into *5-phenyl-2 : 3-dihydrofuran-2 : 3-dicarboxylic acid*, m. p. 182—183°, which by repeated crystallisation from boiling water is converted into α-phenacyl-β-hydroxysuccinic acid (phenacylmalic acid), m. p. 175—176°; the latter acid is reconverted into phenyldihydrofurandicarboxylic acid by repeated crystallisation from a mixture of methyl alcohol and chloroform.

Ethyl *meso*-dibromosuccinate and ethyl sodiobenzoylacetate condense to form as main products ethyl dibenzoylsuccinate and *ethyl α-benzoyltricarballylate*, b. p. 220—225°/12 mm.; this when hydrolysed yields phenacylsuccinic acid, m. p. 162—163°. The *oxime* of phenacylsuccinic acid has m. p. 147—148°; the *phenylhydrazone*, m. p. 164—165°.

Condensation of ethyl *dl*-dibromosuccinate with ethyl sodioacetoacetate gives a 95% yield of *ethyl 5-methyl-2 : 3-dihydrofuran-2 : 3 : 4-tricarboxylate*, b. p. 190—195°/18 mm., which yields on hydrolysis acetonylmalic acid, m. p. 150°, and, on treatment with ammonia, an amide, m. p. 195°. Ethyl diacetosuccinate and ethyl α-acetyltricarballylate, m. p. 110°, result from the condensation of ethyl *meso*-dibromosuccinate and ethyl sodioacetoacetate.

C. J. S.

Hydrated Active Tartaric Acid. M. Amadori (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 507—510).—Crystallisation of aqueous tartaric acid solutions at temperatures below about 5° yields a monohydrated modification, blunt, rhombic prisms, n 1·52, $a : b : c$=0·4706 : 1 : 0·5294. The crystals are stable at temperatures below 5—10°, but at higher temperatures, after turning opaque,

they undergo gradual transformation into transparent crystals of ordinary tartaric acid. T. H. P.

Rotatory Dispersion of Derivatives of Tartaric Acid. I. Methylene Derivatives. P. C. AUSTIN and V. A. CARPENTER (*J. Chem. Soc.*, 1924, **25**, 1939—1946).—The results obtained for the specific rotation of methylene tartaric acid in aqueous solution at different concentrations and for various wave-lengths can be expressed in one term of Drude's equation. The hydrated and anhydrous acids have m. p. 140·5° and 165°, respectively, and the latter has $[\alpha]_D^{20}$ −81·3°.

The rotatory dispersion of dimethylene tartrate can also be expressed in one term of Drude's equation, and the specific rotation appears to be independent of the concentration and the solvent. Dimethylene tartrate has m. p. 119°, $[\alpha]_D^{20}$ +107·9° in ethyl acetate, and on hydrolysis yields a dibasic acid. C. J. S.

Glutaconic Acids. XVI. Three-carbon Tautomerism in the *cyclo*Propane Series. III. Refractometric Evidence. F. R. GOSS, C. K. INGOLD, and J. F. THORPE (*J. Chem. Soc.*, 1924, **125**, 1927—1930).—The authors criticise the conclusions drawn by Auwers and Ottens (this vol., i, 513, 516) from their observations on the exaltations of refractivity exhibited by the esters of the isomeric glutaconic acids, disagree with the view that the isomerism is of geometric character, and consider that the esters belong to the "*cis*" rather than to the "*trans*" type.

Observations of the refractivities of isomeric forms of ethyl 2-methyl-Δ^1-*cyclo*propenedicarboxylate, in which ring formation excludes geometric isomerism, reveal marked exaltations of refractivity, a noteworthy feature being the smaller refractivity of the normal ester. C. J. S.

Behaviour of Formaldehyde. A. FERRINI (*Boll. Chim. Farm.*, 1924, **63**, 467—469).—Determination of the ammoniacal nitrogen in hexamethylenetetramine by simple distillation from a solution rendered alkaline by sodium hydroxide or magnesium, calcium, or barium oxide is not possible, only small proportions of ammonia being liberated in this way. Varying amounts of ammonia, always considerably less than the total amount present, are obtained when a mixture of ammonium chloride and the corresponding quantity of formaldehyde is similarly distilled from an alkaline solution, and still lower results are furnished when the ammonium chloride is replaced by ammonia. Addition of metals having a reducing action does not influence the yield of ammonia in any of the above cases. T. H. P.

Reaction between α-Trioxymethylene and Sulphuryl Chloride. K. FUCHS and E. KATSCHER (*Ber.*, 1924, **57**, [*B*], 1256—1268).—The α-modification of chloroacetic acid, m. p. 56°, is obtained in good yield by heating α-trioxymethylene with sulphuryl chloride and a little zinc chloride at 150—170°. Methyl formate appears to be the primary product of the change, since it is formed in good yield by the action of zinc chloride on α-trioxy

methylene at 125°; it is converted by sulphuryl chloride into chloroacetic acid. Higher alkyl formates do not react similarly; thus ethyl formate yields chloral hydrate (cf. Dunlop, T., 1914, **105**, 1155; Hammick and Boeree, T., 1923, **123**, 2881). H. W.

Relationship of Carboligatic Synthesis to Carboxylatic Degradation (Application of Acetaldehyde as Acceptor). C. Neuberg and O. Rosenthal (*Ber.*, 1924, **57**, [*B*], 1436—1441).—The fermentation of pyruvic acid by zymase solution in the presence of dipotassium hydrogen phosphate leads to the formation of acetaldehyde which is partly transformed into acetylmethylcarbinol, CHMeAc·OH. If, under otherwise identical conditions, acetaldehyde is initially added to the solution, the yield of acetylmethylcarbinol is at least doubled, the generated acetaldehyde being "accepted" by the added reagent and utilised in synthetic directions. H. W.

Polymerisation of Halogenated Derivatives of Ethylene Oxide and of Halogenated Aldehydes. B. Helferich and E. Besler (*Ber.*, 1924, **57**, [*B*], 1276—1280).—The tendency of aldehydes towards trimeric polymerisation is considerably increased by the entry of halogen into the molecule; this does not appear to be the case with derivatives of ethylene oxide.

αβ-Dichlorobutaldehyde, b. p. 48—49°/13 mm. (*semicarbazone*, m. p. 96—97°), is converted by an ethereal solution of magnesium ethyl bromide into βγ-*dichloro*-n-*hexan*-δ-*ol*, b. p. 88—93°/12 mm., d_4^{19} 1·1685, n_D^{19} 1·4709, which is transformed by concentrated potassium hydroxide solution into β-*chloro*-γδ-*oxido*-n-*hexane*, CHMeCl·CH·CHEt, O, b. p. 49—50°/13 mm., d_4^{17} 1·0083, n_D^{17} 1·4310. Similarly, dichlorobutaldehyde and magnesium phenyl bromide yield βγ-*dichloro*-α-*phenylbutan*-α-*ol*, b. p. 162—168°/14 mm., d_4^{15} 1·2355, n_D^{15} 1·5500, which is transformed into γ-*chloro*-αβ-*oxido*-α-*phenylbutane*, b. p. 129—131°/15 mm., d_4^{17} 1·1352, n_D^{17} 1·5325. β-*Chloro*-n-*hexan*-δ-*ol*, b. p. 78—79°/13 mm., d_4^{19} 1·0012, n_D^{19} 1·4433, prepared from β-chlorobutaldehyde and magnesium ethyl bromide, is unchanged by aqueous potassium hydroxide solution (50%) at 40—50°. ββγ-*Trichloro*-α-*phenylbutan*-α-*ol*, b. p. 172—173°/13 mm., m. p. 53°, from butylchloral and magnesium phenyl bromide, is decomposed when treated similarly into benzaldehyde and resin.

Halogenated butaldehydes (1 mol.) condense with acetaldehyde (2 mols.) in the presence of hydrogen chloride at 0° to yield hydroxyl-free products which are regarded as mixed paraldehydes. The following individuals are described: *diacet*-β-*chlorobutparaldehyde*, $O<\begin{matrix}CHMe\cdot O\\CHMe\cdot O\end{matrix}>CH\cdot CH_2\cdot CHMeCl$, b. p. 83—85°/13 mm., d_4^{19} 1·0937, n_D^{19} 1·4373; *diacet*-αβ-*dichlorobutparaldehyde*, b. p. 110—112°/14 mm., $d_4^{17\cdot5}$ 1·2227, $n_D^{17\cdot5}$ 1·4604; *diacet*-ααβ-*trichlorobutparaldehyde*, b. p. 118°/13 mm., d_4^{16} 1·3188, n_D^{16} 1·4739; *diacetchloralparaldehyde*, b. p. 97°/13 mm., d_4^{16} 1·3915, n_D^{16} 1·4708.

Monomeric β-*chlorobutaldehyde*, b. p. 28—33°/13 mm., prepared by the addition of the calculated quantity of hydrogen chloride

to crotonaldehyde in ethereal solution, passes rapidly into the trimeric form. H. W.

Degradation of Pyridine into Glutacondialdehyde and Re-conversion of the Latter into Pyridine. I. P. BAUMGARTEN (*Ber.*, 1924, **57**, [*B*], 1622—1627).—Pyridine is converted by ethyl chlorosulphonate into an additive compound, which is transformed by aqueous sodium hydroxide into sodium sulphamate and the *sodium* salt of the enolic form of glutacondialdehyde, ONa·CH:CH·CH:CH·CHO. The isolation of the salt in two forms, brownish-red crystals and red leaflets, indicates the existence of the aldehyde also in the cyclic form, $CH\ll^{CH—O}_{CH:CH}\gg CH\cdot OH$. The *barium* salt is described. δ-Hydroxy-$\Delta^{\alpha\gamma}$-butadienealdehyde can be preserved unchanged for a short time in ethereal solution, but is too unstable to permit its isolation in substance. The *acetyl* derivative, m. p. 75°, and the *benzoyl* compound, m. p. 116—118°, are described. The latter substance is converted by phenylhydrazine into a *compound*, $C_{18}H_{14}ON_2$, m. p. 149—150°, which has not been identified. As dialdehyde, CHO·CH:CH·CH$_2$·CHO, glutacondialdehyde yields an additive *compound*,

$$C_5H_8O_8S_2Na_2,3H_2O,$$

with sodium hydrogen sulphite (2 mols.). It reacts instantly with phenylhydrazine, but the product could not be crystallised; the *p*-bromophenylhydrazine, $C_{17}H_{16}N_4Br_2$, is an amorphous, reddish-brown powder. The sodium salt of the hydroxyaldehyde is converted by boiling aqueous ammonium acetate into pyridine.

H. W.

Purification of Methyl Ethyl Ketone by Sodium Iodide. H. L. LOCHTE (*Ind. Eng. Chem.*, 1924, **16**, 956).—Methyl ethyl ketone, like acetone (cf. Shipsey and Werner, T., 1898, **103**, 1255), combines with sodium iodide, forming the compound C_4H_8O,NaI. This separates in the crystalline state only when the reagents are slightly moist. It has m. p. 73—74° (decomp., yielding the pure ketone). Commercial samples are best purified by this means.

W. A. S.

Preparation of Higher Ketones. B. HELFERICH and L. KEINER (*Ber.*, 1924, **57**, [*B*], 1616—1620).—The possibility of preparing higher ketones according to the scheme

$$CH_3\cdot C(ONa):CR\cdot CO_2Et \xrightarrow{R^1\cdot COCl} CH_3\cdot CO\cdot CR(CO\cdot R^1)\cdot CO_2Et \longrightarrow R\cdot CH_2\cdot CO\cdot R^1,$$

has been examined. The action of acyl chlorides on the sodium salts leads invariably to the production of a mixture of *O*- and *C*-acyl derivatives, the former of which yields the methyl ketone, $CH_3\cdot CO\cdot CH_2R$, which is obtained also from the alkyl acetoacetate employed. A subsequent separation of the two ketones is therefore essential.

The following acylalkylacetoacetic esters are prepared by dissolving powdered sodium in a solution of the requisite alkylacetoacetic ester in ether and gradually adding the acyl chloride (pre-

pared by means of thionyl chloride) to the ice-cold product: *ethyl* n-*valerylallylacetoacetate*, b. p. 149°/14 mm., $d_4^{16\cdot2}$ 1·0028, n_D^{17} 1·4545; *ethyl* iso*valerylallylacetoacetate*, b. p. 143—144°/14 mm., $d_4^{17\cdot5}$ 0·9998, $n_D^{16\cdot9}$ 1·4546; *ethyl* iso*valerylbenzylacetoacetate*, b. p. 195—196°/14 mm., $d_4^{16\cdot3}$ 1·0524, n_D^{12} 1·5014; *ethyl* Δγ-*pentenoyl*-α-*allylacetoacetate*, $CH_3{\cdot}CO{\cdot}C(CH_2{\cdot}CH{:}CH_2)[CO{\cdot}CH(CH_2{\cdot}CH{:}CH_2)_2]CO_2Et$, b. p. 169—170°/14 mm., $d_4^{16\cdot6}$ 1·0000, n_D^{16} 1·4739; *ethyl* α′-*acetoxypropionylallylacetoacetate*, b. p. 167—168°/14 mm., d_4^{21} 1·0950, $n_D^{19\cdot5}$ 1·4590; *ethyl* p-*acetoxybenzoylallylacetoacetate*, b. p. 235°/14 mm.; *ethyl* o-*acetoxybenzoylallylacetoacetate*, b. p. 216—218°/14 mm.; *ethyl* o-*anisoylallylacetoacetate*, b. p. 219°/18 mm., $d_4^{18\cdot0}$ 1·1376, $n_D^{16\cdot9}$ 1·5300. *Ethyl* α′-*benzoxypropionylallylacetoacetate*, *ethyl trimethylgalloylallylacetoacetate*, and ethyl triacetylgalloylallylacetoacetate could not be distilled without decomposition. For the preparation of *ethyl* β-*chloropropionylallylacetoacetate*, b. p. 158°/14 mm., d_4^{22} 1·1282, n_D^{22} 1·4710, it is necessary to add the alkylsodioacetoacetate to a solution of β-chloropropionyl chloride in ether.

α-*Benzoxypropionyl chloride*, prepared from thionyl chloride and the corresponding acid, has m. p. 23—24° after softening at 21°.

The acylalkylacetoacetates are hydrolysed by potassium hydroxide to the following ketones: n-*butyl* Δγ-*butenyl ketone*, b. p. 72°/14 mm., d_4^{17} 0·8435, n_D^{17} 1·4320 (*semicarbazone*, m. p. 88—89°); iso*butyl* Δγ-*butenyl ketone*, b. p. 62—63°/14 mm., d_4^{12} 0·8362, $n_D^{12\cdot5}$ 1·4288 (*semicarbazone*, m. p. 101—102° after previous softening); p-*hydroxyphenyl* Δγ-*butenyl ketone*, b. p. 210—212°/16 mm., m. p. 61·5° after previous softening; o-*methoxyphenyl* Δγ-*butenyl ketone*, b. p. 152°/16 mm., d_4^{23} 1·0466, n_D^{21} 1·5244; *trimethoxyphenyl* Δγ-*butenyl ketone*, b. p. 195—196°/14 mm., m. p. 54—55° (*semicarbazone*, m. p. 151° after previous softening); *trihydroxyphenyl* Δγ-*butenyl ketone*, m. p. 130° after softening at 120° or (+H_2O) m. p. 84—85° (*semicarbazone*, m. p. 174—175°). The hydrolysis of ethyl *iso*valerylbenzylacetoacetate, ethyl Δγ-pentenoylallylacetoacetate, ethyl α′-acetoxy(benzoxy)propionylallylacetoacetates, and of ethyl β′-chloropropionylallylacetoacetates did not lead to the desired ketone. H. W.

Dihydroxyacetone (II) and a New Method of Preparing Methylglyoxal. H. O. L. Fischer and C. Taube (*Ber.*, 1924, **57**, [*B*], 1502—1507).—In continuation of previous work (Fischer and Mildbrand, this vol., i, 613) monomeric dihydroxyacetone has been converted into its *methyl*cyclo*acetal*, $\begin{matrix}CH_2\\ O\end{matrix}\!\!>\!C(OMe){\cdot}CH_2{\cdot}OH$, m. p. 90—91°. The *acetate* $(C_7H_{12}O_4)_2$, m. p. 109—110°, and the *toluene*-p-*sulphonate*, $C_{12}H_{16}O_5S$, m. p. 117—118° (decomp.), of the corresponding ethyl*cyclo*acetal are described. *Dihydroxyacetonebenzoylhydrazone*, $CH_2(OH){\cdot}C(:N{\cdot}NHBz){\cdot}CH_2{\cdot}OH$, m. p. 133°, *dihydroxyacetone*-p-*nitrophenylhydrazone*, m. p. 156°, and *diacetoxyacetone*-p-*nitrophenylhydrazone*, m. p. 138°, have been prepared. Dihydroxyacetone is fermented by certain varieties of bottom yeast, thus giving the first example of a triose which is fermentable without previous spontaneous conversion into a hexose.

Dihydroxyacetone is converted by distillation with phosphoric oxide into pyruvaldehyde, $CH_3 \cdot CO \cdot CHO$, which is unimolecular in the vaporous state but termolecular in the freshly-prepared, dark green liquid form. When preserved during a few hours, the liquid aldehyde becomes converted into a brittle, resinous mass. It yields a *tetraethylacetal*, $CMe(OEt)_2 \cdot CH(OEt)_2$, b. p. 192°/760 mm., and a *dihydrazone*, m. p. 93—94°. It is converted by methyl chloroformate and potassium cyanide in aqueous solution into *dicarbomethoxymethyltartaronitrile*,

$$CMe(CN)(O \cdot CO_2Me) \cdot CH(O \cdot CO_2Me) \cdot CN,$$

b. p. 100°/0·6 mm., which is hydrolysed by saturated hydrochloric acid at −5° to the corresponding *amide*, m. p. 192°. H. W.

Saturation Relations in Mixtures of Sucrose, Dextrose, and Lævulose. R. F. Jackson and C. G. Silsbee (*U.S. Bur. Standards, Tech. Paper* 259, 277—304).—Invert-sugar diminishes the solubility of sucrose in water, and the solubility of dextrose is decreased by the presence of sucrose or lævulose, although the total sugar content is increased. A mixture of sucrose and invert-sugar saturated with respect to both sucrose and dextrose at 30° contains 33·57% of sucrose and 45·44% of invert-sugar, whilst at 50° the proportions are 27·7% and 58%, such solutions possessing the maximum solubilities that can be attained by partly inverted sucrose solutions. Honey is a supersaturated solution of dextrose in presence of lævulose, and its degree of supersaturation can be calculated in terms of the percentages of dextrose, water, and lævulose. C. J. S.

Acetone [*iso*Propylidene] Derivatives of Sugars and their Derivatives. II. Acetone Compounds of Lævulose. H. Ohle and I. Koller (*Ber.*, 1924, **57**, [*B*], 1566—1576).—Lævulose is converted by acetone in the presence of anhydrous copper sulphate into α-di*iso*propylidenefructose, βγ-*iso*propylidenefructose, and apparently, α-*iso*propylidenefructose. If sulphuric acid is employed in place of copper sulphate, α-di*iso*propylidenefructose, m. p. 118—119°, is mainly produced with small concentrations of acid; with increasing concentration of the latter, the production of β-di*iso*propylidenefructose becomes more pronounced and this substance becomes the main product when the proportion of acid is 4 c.c. per 100 c.c. of acetone. The preparation of β-di*iso*propylidenefructose is effected more economically when lævulose is replaced by sucrose under otherwise identical conditions, whereby a mixture of β-di*iso*propylidenefructose and di*iso*propylideneglucose is formed which is separated into its components by fractional precipitation of its aqueous solution with 10*N*-sodium hydroxide solution. β-Di*iso*propylidenefructose is readily obtained from inulin by means of sulphuric acid and acetone, whereas these reagents do not affect cellulose, starch, maltose, or lactose. It is similarly produced from α-di*iso*propylidenefructose. It has m. p. 97°, b. p. 110—115°/0·175—0·2 mm., $[\alpha]_D^{22}$ −32·9° in water (c = 3·161) $[\alpha]_D^{23}$ −28·98° in benzene, $[\alpha]_D^{21}$ −36·69° in alcohol. It is very much more resistant than the corresponding α-derivative to the hydro-

lysing action of acids (cf. Irvine and Garrett, T., 1910, **97**, 1277). Mainly for this reason, the authors reject the hypothesis of Irvine and his co-workers (*loc. cit.* and T., 1922, **121**, 2146) that the isomeric di*iso*propylidenefructoses are related to one another in the relation of α- to β-glucoside and consider the second *iso*propylidene residue of the β-derivative to be united to the oxygen atoms, 4 and 5; the position of the oxygen bridge is uncertain. *Methyl-β-diisopropylidenefructose* has b. p. 90°/0·12 mm., $n_D^{22\cdot5}$ 1·4512, $[\alpha]_D^{26}$ −35·24° in alcohol. The following acyl derivatives of β-di*iso*propylidenefructose are prepared in the presence of a large excess of pyridine: *acetate*, m. p. 66°, $[\alpha]_D^{25}$ −36·02° in alcoholic solution; *benzoate*, long, thin prisms or coarse, poly-sided crystals, m. p. 81°, $[\alpha]_D^{23}$ −21·8° in alcohol; p-*toluenesulphonate*, m. p. 83°, $[\alpha]_D^{19}$ −27·1° in alcohol.

Since the same product is obtained from dextrose by the action of sulphuric acid in amount varying from 1 to 4 c.c. and acetone (100 c.c.) and its nature is independent of the use of α- or β-glucose as initial material, it appears that di*iso*propylideneglucose is a homogeneous product (contrast Irvine and Patterson, T., 1922, **121**, 2146). This view is confirmed by the observation that di*iso*propylideneglucose under the action of sulphuric acid and acetone is, in part, unchanged and in part transformed into *iso*propylideneglucose without any indication of the production of an isomeride. H. W.

Reversion Synthesis. I. Action of Yeast Maltase. H. Pringsheim and J. Leibowitz (*Ber.*, 1924, **57**, [*B*], 1576—1579).—A solution of dextrose (40%) is subjected to the action of yeast maltase at 37° during four weeks, the optimal hydrogen-ion concentration, p_H =6·4, being used. After fermentation of the residual dextrose by *Saccharomyces Marxianus*, maltose is isolated in the crystalline condition from the portion of the residue soluble in alcohol, whereas slightly impure revertose is obtained from the portion insoluble in alcohol (cf. Croft Hill, T., 1898, **73**, 634; 1903, **83**, 578). The quantity of revertose is much smaller than that of maltose, whereas the reverse is the case in Croft Hill's experiments. H. W.

Products of the Enzymic Fission of Starch. K. Sjöberg (*Ber.*, 1924, **57**, [*B*], 1251—1256).—The action of undialysed malt amylase solution on amylose followed by precipitation of the product with alcohol (80%) leads to the isolation of a dihexosan, $[\alpha]_{Hg\ yellow}^{18}$ +154·5 to 155·7° in water, probably identical with the product described by Pringsheim and Wolfsohn (this vol., i, 714), which readily yields *dihexosan hexa-acetate*, m. p. 150—165°, $[\alpha]_{Hg\ yellow}^{18}$ +124·6° in acetic anhydride, $[\alpha]_{Hg\ yellow}^{18}$ +123·5° in pyridine, but is only converted by methyl iodide and silver oxide into *tetramethyldihexosan*, $[\alpha]_{Hg\ yellow}^{18}$ +144·9°, from which βγ-dimethylglucose is obtained on hydrolysis. Amylopectin, when similarly treated, yields a trihexosan, $[\alpha]_{Hg\ yellow}^{18}$ +162·9 to 164·0° in water, probably identical with the compound prepared by Pictet and Jahn (A., 1922, i 987) by heating potato starch in glycerol

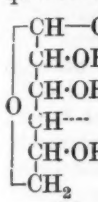
at 200—210°; the corresponding nona-acetate has m. p. 156—165°, $[\alpha]^{18}_{Hg\ yellow}$ +131·4° in acetic anhydride, $[\alpha]^{18}_{Hg\ yellow}$ +132·9° in pyridine. H. W.

Starch. XI. Halogen Compounds of the Polyamyloses. H. PRINGSHEIM and A. STEINGROEVER (*Ber.*, 1924, **57**, [*B*], 1579—1581).—Re-examination of the additive compounds of bromine with the polyamyloses (cf. Pringsheim and Eissler, A., 1913, i, 1156; 1915, i, 382) shows them to contain combined in addition to free bromine, so that in this respect they resemble the starch iodides (this vol., i, 618, 837). It does not, however, appear possible to establish a relationship between free and total halogen in the polyamyloses or to detect in their ash an amount of base corresponding with the amount of combined halogen. Bromo-α-hexa-amylose has approximately the composition $(C_6H_{10}O_5)_6Br_2$. Tri-amylose combines with about 2% more bromine than does hexa-amylose. H. W.

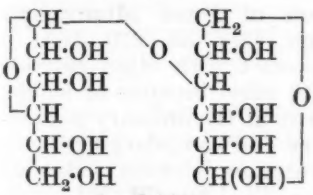
Starch. XII. Constitution of Starch, Glycogen, and Lichen Starch. H. PRINGSHEIM [with A. BEISER, K. WOLFSOHN, L. LEIBOWITZ, and W. KUSENACK] (*Ber.*, 1924, **57**, [*B*], 1581—1598).—Further evidence of the difference in constitution of the content- and integument-substances of the starch granule (cf. this vol., i, 714) is afforded by the observation that the former is converted by cold, concentrated hydrochloric acid into *amylobiose*, $C_{12}H_{22}O_{11}$, $[\alpha]^{20}_D$ +110·9° in aqueous solution, whereas the latter yields *amylotriose*, $C_{18}H_{32}O_{16}$, $[\alpha]^{20}_D$ +124·5° in water (*osazone*, decomp. 142—145°). Under the influence of amylases, amylose is quantitatively converted into maltose, whereas reaction ceases when 65% of amylopectin has been transformed into this sugar; the unattacked residue is identified as trihexosan which, since it can be further fermented with undialysed malt extract, appears to be, not an essential component of the amylopectin molecule, but an accidental residue. The two components occur separately in nature, since amylose is shown to be identical with *iso*lichenin (Pringsheim and Kusenack, this vol., i, 1144) obtained from Iceland moss, which is fermented quantitatively to maltose by fresh malt extract, transformed when heated in glycerol at 185—190° into dihexosan, and hydrolysed by cold, concentrated hydrochloric acid to amylobiose. Amylopectin is identified with glycogen, which is transformed by cold, concentrated hydrochloric acid into amylotriose. The identity of the disaccharide obtained from α-tetra- and β-hexa-amylose and hydrochloric acid (Pringsheim and Leibowitz, this vol., i, 714) with amylobiose is also established.

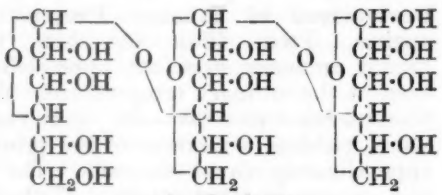
The two-enzyme theory of the amylases (Pringsheim, "Die Polysaccharide," 1923, p. 141) renders account of the liquefaction, caused by fermentative fission of electrolyte, and of the saccharification which can be distinguished by the poisoning of malt amylase. A third type of action, consisting in the depolymerisation of the starch molecule to the non-reducing hexosans, appears to take place intermediately. Since the action consists in the rupture of the amylobiose linking, the enzyme complex is termed amylobiase.

Amylobiose, amylotriose, and di- and tri-hexosans are converted quantitatively by malt amylase into maltose; the experimental work is complicated by the unexpected observation that maltose in 1% solution at 37° is slowly converted into dextrose at the acidity (p_H 4·5) which is optimal for malt amylase. They are not attacked by the α-glucosidic maltase or the β-glucosidic enzyme of emulsin. The surprising fermentative production of a biose from a different biose or a triose, which has nothing in common with the reversible, synthetic action of enzymes, is most readily explained by the hypothesis that a glucose residue (I), probably as a consequence of the nature of its oxygen bridge, is eliminated as a radical which unites with another similar group to yield maltose.


(I.)

The quantitative formation of maltose from amylobiose renders the formula proposed previously (Pringsheim and Leibowitz, (*loc. cit.*) untenable. The following constitutions are proposed for amylobiose and amylotriose:


Amylobiose.


Amylotriose.

It is suggested that the formaldehyde formed during the assimilation of carbon dioxide by plants passes immediately into the author's radical, from which the content- and integument-substances of the starch granule are produced directly. H. W.

Carbonic Esters of Cellulose. E. Heuser and F. Schneider (*Ber.*, 1924, **57**, [*B*], 1389—1392).—The action of an excess of methyl chloroformate on a solution of hydrocellulose in cold aqueous sodium hydroxide (8%) gives *esters* which approximate very closely to the formula $C_6H_8O_3(O{\cdot}CO_2Me)_2$. They form a white, amorphous, granular material, soluble in pyridine, chloroform, and acetic acid. They are readily hydrolysed. Analysis of them is effected by determining carbon dioxide and methoxyl content. H. W.

Mannan Content of Wood-cellulose and its Analytical Determination. E. Heuser and W. Dammel (*Cellulosechem.*, 1924, **5**, 45—53).—The mannan in the cellulose from coniferous woods is determined by Schorger's method (*J. Ind. Eng. Chem.*, 1917, **9**, 748) after hydrolysis with hydrochloric acid by precipitation in the form of mannose bromophenylhydrazone. Mannan is extracted by treating the pulp with 17% aqueous sodium hydroxide, but the exhaustion is not always complete even after two or three treatments. It is determined after hydrolysis of the extract, but Schorger's method by direct hydrolysis of the pulp is to be preferred.

On acidification of the alkaline extract and precipitation with alcohol, a portion of the mannan is found in the precipitated hemicellulose, but a further portion remains in the filtrate. The pentosans behave in a similar manner, being distributed in unequal portions in the α-, β-, and γ-cellulose fractions. There is no support for the suggestion that the mannose forms an integral component of the wood cellulose molecule. The statement of Lenze, Pleus, and Müller (*J. pr. Chem.*, 1922, **101**, 213) that when the β-cellulose from wood pulp is boiled with 4% nitric acid, the hemicelluloses are completely hydrolysed, leaving a residue of oxycellulose, is not accepted as the basis of a valid method for the determination of oxycellulose in wood pulp. In the first place, the oxycellulose is not quantitatively present in the β-cellulose fraction, and, secondly, the hydrolysis is not quantitatively selective. The phenylhydrazone indicated by those authors as that of methylfurfuraldehyde is proved to be that of hydroxymethylfurfuraldehyde derived from dextrose. J. F. B.

Action of Liquid Ammonia and Sodamide on Halogen Derivatives of Ethane. Preparation of Pure Monoethylamine. Picon (*Bull. Soc. chim.*, 1924, [iv], **35**, 979—981).—Liquid ammonia does not appreciably react with ethyl chloride even at the ordinary temperature. With ethyl bromide or iodide, reaction takes place at −40°, more rapidly at the ordinary temperature, yielding a mixture of the primary and secondary amine in approximately equal amounts. The reaction between sodamide and potassium ethyl sulphate (Titherley, T., 1901, **79**, 391) gives very poor yields of ethylamine, owing to the large quantity of ethylene and ammonia produced. In the presence of liquid ammonia, at the ordinary temperature, sodamide yields a mixture of primary, secondary, and tertiary amine with ethyl bromide or iodide, some ethylene being also formed, but with ethyl chloride pure ethylamine is obtained. The yield amounts to only 30% of the theoretical, owing to the formation of a considerable quantity of ethylene. R. B.

Mechanism of Oxidation Processes. VIII. Scission by Oxidation of Amino-acids. H. Wieland and F. Bergel (*Annalen*, 1924, **439**, 196—210; cf. this vol., i, 606).—Glycine, alanine, and phenylalanine are oxidised by gaseous oxygen in presence of active charcoal at 38° to carbon dioxide, ammonia (in equimolecular proportions), an aldehyde with one carbon atom less than the original acid, and a little of the corresponding acid. Aspartic acid gives 2 mols. of carbon dioxide to 1 mol. of ammonia. α-Iminopropionic acid gives carbon dioxide, ammonia, and acetaldehyde; α-amino*iso*butyric acid is unaffected. The free oxygen may be replaced by alloxan, *m*-dinitrobenzene, dithioglycollic acid, or *p*-benzoquinone. Succinic acid is dehydrogenated by dithioglycollic acid in presence of freshly-minced liver. These experimental results provide new material for an exhaustive discussion of the mechanism involved in the disruption of α-amino-acids.
W. A. S.

Steric Series. IV. Configuration of Alanine. K. FREUDENBERG and F. RHINO (*Ber.*, 1924, **57**, [*B*], 1547—1557; cf. A., 1923, i, 215).—Basing the work on the hypothesis that analogous compounds of like configuration suffer corresponding changes in optical rotation under similar conditions (cf. Clough, T., 1918, **113**, 526), an examination of lactic acid and alanine has been made. To obtain constants free from external influences it is necessary to avoid the presence of free hydroxy, carboxy, or amino groups and to determine the rotations of the liquid or molten substances. Where this is impossible, the rotation is obtained by extrapolation from a series of solutions of different and ultimately very high concentration. In cases of doubt, several solvents are employed, the choice falling on those in which the rotation of the dissolved substance is least dependent on the concentration. The elimination of the use of a solvent is the most important feature of the whole problem, since variations in rotation due to solvent are of very much greater magnitude than those due to temperature. The abnormalities due to rotatory dispersion also become less in evidence. The measurements are effected for light of four different wave-lengths. Comparison of the different compounds with one another is based on the values of K_M deduced from the equation

$$(\lambda_n^2-\lambda_0^2)\,.\,[M]_n=K_M,$$

where M is the molecular rotation (cf. Rupe and Ackermann, A., 1920, ii, 652). It is thus established that *l*-lactic acid has the same configuration as natural *d*-alanine. From the point of view of the Walden inversion, the action of nitrous acid on alanine, serine, and aspartic acid occurs, therefore, without inversion, since these compounds yield hydroxy-acids belonging to the *l*-series.

The following compounds are incidentally described; the specific rotations are recorded for the wave-lengths 649, 578, 546, and 444 $\mu\mu$: *ethyl* d-α-*acetoxypropionate*, b. p. 170—172°/760 mm.; *ethyl* r-α-*hexahydrobenzoxypropionate*, b. p. 132—135°/13 mm., and the corresponding d-*ester*; methyl r-α-*benzoxypropionate*, b. p. 144—145°/13 mm., 275—280°/760 mm., and the corresponding *ethyl* ester, b. p. 150°/12 mm., 282°/760 mm., and the similar d-*compounds*. *r*-α-Benzoxypropionamide, m. p. 116—117°; *methyl* r-p-*toluenesulphonoxypropionate*, b. p. 170—173°/0·5 mm.; *ethyl* d-p-*toluenesulphonoxypropionate*, b. p. 175—177°/0·5 mm.; *ethyl* r-p-*toluenesulphonoxypropionate*, b. p. 175—177°/0·5 mm.; r-α-p-*toluenesulphonoxypropionamide*, m. p. 87—88°, and the corresponding d-*amide*, m. p. 105°; ethyl *dl*-α-acetamidopropionate, m. p. 39°, and the corresponding *l*-ester, m. p. 34—35°; *ethyl* r-α-*hexahydrobenzamidopropionate*, from the components in the presence of pyridine, m. p. 77—78°; *ethyl* l-α-*hexahydrobenzamidopropionate*, m. p. 75°; *methyl* l-α-*benzoylaminopropionate*, m. p. 58°; *ethyl* l-α-*benzamidopropionate*, m. p. 97—98°; l-α-*benzamidopropionamide*, m. p. 228—229°; l-α-p-*toluenesulphonamidopropionamide*, m. p. 212—213°; *ethyl* l-α-p-*toluenesulphonamidopropionate*. H. W.

Preparation of Melanins containing Sulphur. O. ADLER (*Biochem. Z.*, 1924, **148**, 541—547).—Using the method already

On acidification of the alkaline extract and precipitation with alcohol, a portion of the mannan is found in the precipitated hemicellulose, but a further portion remains in the filtrate. The pentosans behave in a similar manner, being distributed in unequal portions in the α-, β-, and γ-cellulose fractions. There is no support for the suggestion that the mannose forms an integral component of the wood cellulose molecule. The statement of Lenze, Pleus, and Müller (*J. pr. Chem.*, 1922, **101**, 213) that when the β-cellulose from wood pulp is boiled with 4% nitric acid, the hemicelluloses are completely hydrolysed, leaving a residue of oxycellulose, is not accepted as the basis of a valid method for the determination of oxycellulose in wood pulp. In the first place, the oxycellulose is not quantitatively present in the β-cellulose fraction, and, secondly, the hydrolysis is not quantitatively selective. The phenylhydrazone indicated by those authors as that of methylfurfuraldehyde is proved to be that of hydroxymethylfurfuraldehyde derived from dextrose. J. F. B.

Action of Liquid Ammonia and Sodamide on Halogen Derivatives of Ethane. Preparation of Pure Monoethylamine. Picon (*Bull. Soc. chim.*, 1924, [iv], **35**, 979—981).—Liquid ammonia does not appreciably react with ethyl chloride even at the ordinary temperature. With ethyl bromide or iodide, reaction takes place at −40°, more rapidly at the ordinary temperature, yielding a mixture of the primary and secondary amine in approximately equal amounts. The reaction between sodamide and potassium ethyl sulphate (Titherley, T., 1901, **79**, 391) gives very poor yields of ethylamine, owing to the large quantity of ethylene and ammonia produced. In the presence of liquid ammonia, at the ordinary temperature, sodamide yields a mixture of primary, secondary, and tertiary amine with ethyl bromide or iodide, some ethylene being also formed, but with ethyl chloride pure ethylamine is obtained. The yield amounts to only 30% of the theoretical, owing to the formation of a considerable quantity of ethylene. R. B.

Mechanism of Oxidation Processes. VIII. Scission by Oxidation of Amino-acids. H. Wieland and F. Bergel (*Annalen*, 1924, **439**, 196—210; cf. this vol., i, 606).—Glycine, alanine, and phenylalanine are oxidised by gaseous oxygen in presence of active charcoal at 38° to carbon dioxide, ammonia (in equimolecular proportions), an aldehyde with one carbon atom less than the original acid, and a little of the corresponding acid. Aspartic acid gives 2 mols. of carbon dioxide to 1 mol. of ammonia. α-Iminopropionic acid gives carbon dioxide, ammonia, and acetaldehyde; α-amino*iso*butyric acid is unaffected. The free oxygen may be replaced by alloxan, *m*-dinitrobenzene, dithioglycollic acid, or *p*-benzoquinone. Succinic acid is dehydrogenated by dithioglycollic acid in presence of freshly-minced liver. These experimental results provide new material for an exhaustive discussion of the mechanism involved in the disruption of α-amino-acids. W. A. S.

Steric Series. IV. Configuration of Alanine. K. FREUDENBERG and F. RHINO (*Ber.*, 1924, **57**, [*B*], 1547—1557; cf. A., 1923, i, 215).—Basing the work on the hypothesis that analogous compounds of like configuration suffer corresponding changes in optical rotation under similar conditions (cf. Clough, T., 1918, **113**, 526), an examination of lactic acid and alanine has been made. To obtain constants free from external influences it is necessary to avoid the presence of free hydroxy, carboxy, or amino groups and to determine the rotations of the liquid or molten substances. Where this is impossible, the rotation is obtained by extrapolation from a series of solutions of different and ultimately very high concentration. In cases of doubt, several solvents are employed, the choice falling on those in which the rotation of the dissolved substance is least dependent on the concentration. The elimination of the use of a solvent is the most important feature of the whole problem, since variations in rotation due to solvent are of very much greater magnitude than those due to temperature. The abnormalities due to rotatory dispersion also become less in evidence. The measurements are effected for light of four different wave-lengths. Comparison of the different compounds with one another is based on the values of K_M deduced from the equation

$$(\lambda_n^2-\lambda_0^2)\cdot[M]_n=K_M,$$

where M is the molecular rotation (cf. Rupe and Ackermann, A., 1920, ii, 652). It is thus established that *l*-lactic acid has the same configuration as natural *d*-alanine. From the point of view of the Walden inversion, the action of nitrous acid on alanine, serine, and aspartic acid occurs, therefore, without inversion, since these compounds yield hydroxy-acids belonging to the *l*-series.

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Preparation of Melanins containing Sulphur. O. ADLER (*Biochem. Z.*, 1924, **148**, 541—547).—Using the method already

described (A., 1923, i, 591, 1218), *tyrosinesulphomelanic acid*, a dark grey, hygroscopic, amorphous powder, has been prepared from tyrosinesulphonic acid. The *sodium* and *barium* salts are described. By heating at 270° for 2 hours, the acid is converted into *tyrosinesulphomelanin*, a black, hygroscopic powder. Similarly, from thiophen, *thiophenmelanic acid*, a dark, amorphous powder, and *thiophenemelanin*, a black powder, were obtained.

J. P.

Action of Triphenylmethyl Chloride on Ethyl β-Aminocrotonate and Analogous Compounds. E. BENARY and P. LORTH.—(See i, 1192.)

Complexes of Carbamide with Cadmium Salts. L. BELLADEN and A. CIAMPA (*Gazzetta*, 1924, **54**, 568—571).—The following complex *compounds* are described: $CdCl_2,CO(NH_2)_2$; $CdCl_2,2CO(NH_2)_2$; $CdBr_2,CO(NH_2)_2$ and $CdBr_2,2CO(NH_2)_2$; $CdI_2,CO(NH_2)_2$ and $CdI_2,2CO(NH_2)_2$; $Cd(ClO_4)_2,6CO(NH_2)_2$; $Cd(SCN)_2,2CO(NH_2)_2$. The results of cryoscopic and conductivity measurements show that, in aqueous solution, these complex compounds undergo complete dissociation into their components.

T. H. P.

Electrolysis of Aqueous Solutions of Cyanamide. N. KAMEYAMA (*J. Coll. Eng. Tokyo*, 1924, **13**, 271—310).—The electrolytic oxidation and reduction of aqueous solutions of cyanamide, acidified with sulphuric acid, sodium acetate, and acetic acid, in the presence of potassium sulphate, and, in the case of oxidation, in alkaline solution, and of solutions of acid calcium cyanamide, $Ca(CN_2H)_2$, using lead, mercury, cadmium, zinc, and platinum cathodes, was studied at the ordinary or a slightly elevated temperature. Electrolytic reduction follows the same course as that produced by nascent hydrogen, methylamine and ammonia being produced. The intermediate formation of hydrogen cyanide could not be detected. The highest current efficiencies obtained were 10—20% with the cadmium cathode in the cyanamide solution containing sodium acetate and acetic acid or in the acid calcium cyanamide solution. Electrolysis of cyanamide solution without the separation of anodic and cathodic compartments yielded a trace of cyanide in acidic or neutral solutions, and a larger quantity, together with some cyanate, in alkaline solutions. On anodic oxidation, using a Pukall diaphragm and a platinum anode, the cyanamide solution became first yellow, then reddish-orange, and at this stage, on standing over-night, the solution deposited an orange-red, crystalline compound containing nitrogen. On continued electrolysis, the solution became pale yellow again and finally colourless. Electrolysis of the cyanamide in alkaline solution without a diaphragm yielded cyanide. Preliminary experiments on the anodic oxidation of cyanamide in alkaline solution showed the production of cyanate in solution and the evolution of nitrogen.

J. W. B.

Conversion of Calcium Cyanamide into Cyanides. J. DODONOW (*Ann. Inst. agron. Saratow*, 1922, **1**, 1–13; from *Chem. Zentr.*, 1924, ii, 317–318).—When a mixture of calcium cyanamide (160 g.), sodium carbonate (125 g.), and wood charcoal (32 g.) was added gradually to 20 g. of sodium carbonate heated to bright redness, and the temperature maintained for 20 mins., 63·5 g. of sodium cyanide (78% yield on the nitrogen of the cyanamide) were obtained; with potassium carbonate the yield was 70%. By heating calcium cyanamide with excess of water at 60°, dicyanodiamide was produced in 82% yield, together with carbamide (7%); boiling with water gave a 60% yield.

Hydrazidicarbonazide and its Formation as By-product of the Diazotisation of Carbohydrazide. W. KESTING (*Ber.*, 1924, **57**, [*B*], 1321—1324).—The addition of hydrochloric acid to an aqueous solution of carbohydrazide and sodium nitrite in the presence of light petroleum, b. p. 98°, leads to the formation of carboazide, $CO(N_3)_2$, which passes into the light petroleum, and hydrazidicarbonazide, $N_2H_2(CO{\cdot}N_3)_2$, which remains in the aqueous layer (cf. Stollé and Krauch, A., 1914, i, 592). The latter substance, m. p. 150—152° (decomp.) when slowly heated, is highly explosive. With piperidine, *hydrazidicarbonpiperidide*, $N_2H_2(CO{\cdot}NC_5H_{10})_2$, m. p. 179°, is formed. H. W.

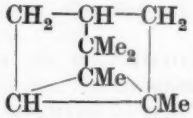
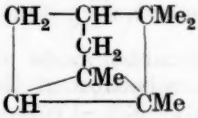
Action of Ammonium Hydroxide on Copper Ferrocyanide. E. D. CRITTENDEN (*J. Amer. Chem. Soc.*, 1924, **46**, 1210—1211).—Copper ferrocyanide does not dissolve in ammonia solution, but forms a silky, brown solid which probably has the formula $Cu_2Fe(CN)_6,4NH_3$. The presence of a trace of ammonia seriously impairs the delicacy of the ferrocyanide test for small quantities of copper. M. S. B.

Nitrogenous Condensation Products from Acetylene and Ammonia. CHEM. FABR. RHENANIA (D.R.-P. 382091; from *Chem. Zentr.*, 1924, i, 2298—2399).—Acetylene and ammonia react in the presence of water vapour and a hydrated substance, such as aluminium hydroxide, forming under different conditions acetonitrile, picoline, aldehyde-ammonia, ethylamine, and nitrogenous bases of high molecular weight. The principal product is acetonitrile. G. W. R.

Application of Zelinsky's Method of Catalytic Dehydrogenation to the Detection of Decahydronaphthalenes in Low-temperature Tar. H. KAFFER (*Ber.*, 1924, **57**, [*B*], 1261—1265).—Suitable fractions of low-temperature tar are freed from aromatic hydrocarbons by treatment with sulphuric acid and dehydrogenated by repeated passage at 320—330° over platinised charcoal which has been activated by contact with oxygen at the atmospheric temperature. The products are treated with sulphuric acid and the sulphonic acids are decomposed into the corresponding hydrocarbons by means of superheated steam. Naphthalene, 1-methyl- and 1 : 6-dimethyl-naphthalene are thereby isolated,

thus establishing the presence of the corresponding decahydro compounds in the tar. Activated platinised charcoal is a more active catalyst than platinised asbestos. H. W.

Methylcyclene. S. Nametkin and L. Brüssoff (*Ber.*, 1924, **57**, [*B*], 1258—1260).—6-Methylcamphor is converted by hydrazine hydrate at 180—190° into a mixture of the corresponding *hydrazone*, b. p. 153—154°/42 mm., m. p. 103—105°, and *azine*, m. p. 131—133°. The hydrazone is oxidised by mercuric oxide to *methylcyclene* (I or II), b. p. 168—168·5°/762 mm., m. p. 110·5—111°.

(I.)  (II.) 

The new hydrocarbon is not identical with the product of the dehydration of *tert.*-methylfenchol or *tert.*-methylborneol (Bredt, A., 1919, i, 125). H. W.

Hydrolysis of the *p*-Toluenesulphonchloroamides in Water. F. G. Soper (*J. Chem. Soc.*, 1924, **125**, 1899—1910).—In aqueous solution, *p*-toluenesulphondichloroamide is hydrolysed into hypochlorous acid (cf. Selivanov, A., 1893, i, 192) and the monochloroamide: $C_7H_7\cdot SO_2\cdot NCl_2 + H_2O \rightleftharpoons C_7H_7\cdot SO_2\cdot NHCl + HOCl$, the existence of the latter, which could not be isolated, being indicated by the greater solubility of the dichloroamide in solutions of the sulphonamide than in water. The monochloroamide probably exists as an equilibrium mixture of the two isomerides,

$$C_7H_7\cdot SO_2\cdot NHCl$$

and $C_7H_7\cdot SO_2H{:}NCl$, hydrolysis of the monochloroamide from equimolecular quantities of the sulphonamide and hypochlorous acid and from acidification of "chloramine-T" (sodium salt of the monochloroamide), yielding identical results. From determinations of the solubility of the dichloroamide in solutions of the sulphonamide (cf. Löwenherz, A., 1898, ii, 326) and of the free chlorine in solutions of "chloramine-T" acidified with hydrochloric acid (cf. Orton and Jones, T., 1909, **95**, 1456) the equilibrium constants of the hydrolysis of mono- and di-chloroamides of *p*-toluenesulphonamide in water at 25° have been calculated as $4{\cdot}9 \times 10^{-8}$ and $8{\cdot}0 \times 10^{-7}$, respectively. The concentration of hypochlorous acid in solutions of acidified "chloramine-T" is independent of the concentration of the "chloramine-T." R. B.

Nitro-*p*-*tert.*-butyltoluene. M. Battegay and P. Haeffely (*Bull. Soc. chim.*, 1924, [iv], **35**, 981—988).—Nitration of *p*-*tert.*-butyltoluene with nitric and sulphuric acids at 5—10° gives 2-*nitro*-p-tert.-*butyltoluene*, a yellow oil, volatile in steam, b. p. 138—139°/13 mm., having a slight odour of musk. Its constitution is proved by the following series of reactions. On oxidation in pyridine with potassium permanganate it gives o-*nitro*-p-tert.-*butylbenzoic acid*, m. p. 145°, which on reduction in dilute ammonia with ferrous sul-

phate yields o-*amino*-p-tert.-*butylbenzoic acid*, m. p. 174°. The amino-acid, by treatment with potassium cyanide and formaldehyde in benzene suspension, followed by hydrolysis with sodium hydroxide, is converted into p-tert.-*butylphenylglycine*-o-*carboxylic acid*, m. p. 246°, and the sodium salt of the glycinecarboxylic acid on fusion with sodium and potassium hydroxides at 270° yields 6 : 6′-*dibutylindigotin*, violet needles, a reaction which proves the position of the nitro-group. On reduction, 2-nitro-*p-tert.*-butyltoluene yields p-tert.-*butyl*-o-*toluidine*, b. p. 128—129°/13 mm., volatile in steam (*hydrochloride*; *acetyl* derivative, m. p. 112°; *benzoyl* derivative, m. p. 143°; *toluene*-p-*sulphonyl* derivative, m. p. 158°), converted by the diazo reaction into p-tert.-*butyl*-o-*cresol*, a viscous oil, which on treatment with nitrous acid gives, besides traces of a nitrogenous substance, m. p. 172°, p-tert.-*butyltoluquinone*, golden-yellow spangles, m. p. 95°, volatile in steam and possessing a powerful quinone-like odour. On further nitration at 30° with fuming nitric and sulphuric acids, 2-nitro-*p-tert.*-butyltoluene gives, in 90% of the theoretical yield, the 2 : 6-dinitro-*p-tert.*-butyltoluene, m. p. 94—95°, obtained by Bialobrzeski (A., 1897, i, 514), the constitution of which follows from its reduction to p-tert.-*butyl*-2 : 6-*tolylenediamine*. R. B.

Artificial Musks. M. Battegay and M. Kappeler (*Bull. Soc. chim.*, 1924, [iv], **35**, 989—996).—With a view to obtain evidence as to whether the odour of artificial musk (trinitro-*tert.*-butyl-*m*-xylene) is due to the specific influence of the tertiary butyl group as such or merely to the tertiary carbon atom which it contains, a number of analogous derivatives of *m*-xylene have been prepared and the properties of their nitro derivatives examined. Replacement of the *tert.*-butyl group by *cyclo*hexyl leads to an odourless trinitro compound; *tert.*-heptyl-*m*-xylene (*m*-xylyltriethylmethane) yields a nitration product with a strong but somewhat disagreeable odour of musk, whilst 5-triphenylmethyl-*m*-xylene yields only odourless nitration products, and it is concluded that both the tertiary carbon atom and the butyl radical as such exert an " osmophoric " influence.

m-Xylene and *cyclo*hexyl bromide condense in the presence of ferric or aluminium chloride, yielding a *dicyclohexyl*-m-*xylene*, $C_{20}H_{30}$, m. p. 104°, and 5-cyclo*hexyl*-m-*xylene*, b. p. 265—266°/748 mm., 142—143°/17 mm., with an odour of geranium, which on nitration with nitric and fuming sulphuric acids gives 2 : 4 : 6-*trinitro*-5-cyclo*hexyl*-m-*xylene*, m. p. 117—118°, the constitution of which follows from its synthesis by nitrating the hydrocarbon obtained by deaminating the condensation product of *cyclo*hexyl bromide and 2-*m*-xylidine hydrochloride. Similarly, *m*-xylene and methyldiethylethylene (Saytzeff, A., 1898, i, 289) in the presence of aluminium chloride readily yield 5-αα-*diethylpropyl*-m-*xylene*, b. p. 257—259°/745 mm., which on nitration with nitric and sulphuric acids yields only trinitro-*m*-xylene, whilst with nitric acid and acetic anhydride an oily product of musk-like odour is obtained. Triphenylcarbinol and 2-*m*-xylidine hydrochloride in boiling acetic

acid yield 5-*triphenylmethyl*-2-m-*xylidine hydrochloride*, a red powder, m. p. 277—278°; the free *base* has m. p. 177°. On diazotisation of the sulphate in acetic acid solution with amyl nitrite and decomposition of the *diazonium* salt with absolute alcohol in the presence of copper, 5-*triphenylmethyl*-m-*xylene*, m. p. 154°, b. p. 450°, is obtained. No definite nitration product was obtained. R. B.

Sulpho Derivatives of Acenaphthene. K. Dziewoński and T. Stolyhwo (*Ber.*, 1924, **57**, [*B*], 1531—1540).—Acenaphthene-5-sulphonic acid (cf. Oliveri-Mandala, *Rend. Accad. Lincei*, 1912, 779) is conveniently prepared by the action of sulphuric acid (8 g.) on acenaphthene (10 g.) at 100°, and is readily separated as the sodium salt; the ethyl ester, m. p. 87—88°, and the *amide*, m. p. 196—199°, are described. The sodium salt is transformed when heated with potassium ferrocyanide, potassium cyanide, or potassium hydroxide into acenaphthylene and polyacenaphthylene. Acenaphthene-3-sulphonic acid (described erroneously in D.R.-P. 248994 as the 1-sulphonic acid because of its conversion by fused potassium hydroxide into acenaphthylene) is obtained by the addition of sulphuric acid (100%) or chlorosulphonic acid to a solution of acenaphthene in nitrobenzene at 0—20°. The *sodium* and *barium* salts are described. *Acenaphthene-3-sulphonyl chloride* is readily converted into *acenaphthene-3-sulphonamide*, m. p. 222—223°, and *ethyl acenaphthene-3-sulphonate*, m. p. 137—139°. Attempts to prepare the corresponding nitrile from the sulphonate yielded only acenaphthylene and its polymeride. The constitution of the acid is established by its oxidation with sodium dichromate in glacial acetic acid solution to 2-sulphonaphthalene-1 : 8-dicarboxylic acid (the *sodium hydrogen* salt and the *barium* salt are described); the acid is converted by fused potassium hydroxide into 2-naphthol-1 : 8-dicarboxylic acid (cf. Dziewoński and Stolyhwo, this vol., i, 1199).

Treatment of acenaphthene with an excess of concentrated or with fuming sulphuric acid leads to the formation of disulphonic acids of which two, termed provisionally α- and β-acid, have been isolated. In contrast to the monosulphonic acids they yield barium salts which dissolve very freely in water and are adapted to their isolation. *Acenaphthene-α-disulphonic* acid is prepared from the hydrocarbon (10 g.) and concentrated sulphuric acid (20 g.) at 100°; the *sodium* and *barium* salts and the *disulphonyl chloride* are described. *Acenaphthene-α-disulphonamide* and *methyl acenaphthene-α-disulphonate* have m. p. 282° (decomp.) and 170—171°, respectively. The acid is readily nitrated to a nitroacenaphthene-α-disulphonic acid which is isolated as the *sodium* salt. Acenaphthene (10 g.) is converted by cold concentrated sulphuric acid (50 g.) into acenaphthene-β-disulphonic acid [*barium* and *sodium* salts; *sulphonyl chloride*; *acenaphthene-β-disulphonamide*, m. p. 301° (decomp.)]. Desulphonation of either acenaphthenedisulphonic acid gives primarily acenaphthene-5-monosulphonic acid and ultimately acenaphthene; in each case one of the two sulphonic groups must occupy position 5. H. W.

Complex Isomerism. E. Hertel (*Ber.*, 1924, **57**, [*B*], 1559—1561).—o-*Bromoaniline picrate* exists in two forms, long, red needles, m. p. 128·5°, obtained by allowing a solution of the components in chlorobenzene to crystallise above 95°, and a yellow variety prepared in alcoholic solution. It therefore appears to fulfil the predictions of Pfeiffer ("Organische Molekülverbindungen," 1922, p. 226) with regard to the existence of two types of picrate, in one of which the hydroxylic hydrogen of picric acid is united by a subsidiary valency to the basic nitrogen atom ("true picrates"), whereas in the other the subsidiary valency of the nitro group of picric acid is saturated by the valency field produced by the residual affinities of the aromatic nucleus of the base, $OH{\cdot}C_6H_2(NO_2)_3...RNH_2$. When picric acid is triturated with *o*-bromoaniline, a carmine-red mixture is obtained which becomes yellow slowly at the atmospheric temperature, instantaneously at 65°; a similar, irreversible effect is produced immediately by the vapours of ether, acetone, or ethyl acetate. Analogous observations are made with *o*-bromoaniline and trinitrobenzene. *Picrates* of the following bases are described incidentally: m-*bromoaniline*, m. p. 180°; p-*bromoaniline*, m. p. 180°; o-, m-, and p-*chloroanilines*, m. p. 134°, 177°, and 178°, respectively; 2 : 4-*dichloroaniline*, m. p. 106°; 2 : 4-*dibromoaniline*, m. p. 124°; 2 : 6-*dibromoaniline*, m. p. 123—124° (the molten product solidifies when quickly cooled to a red mass, m. p. 95°); 2 : 4 : 6-*tribromoaniline*. H. W.

Acetoacetanilide. C. Bülow and E. King (*Annalen*, 1924, **439**, 211—220).—α-*Chloroacetoacetanilide*, m. p. 137·5°, is produced by the interaction of sulphuryl chloride and acetoacetanilide in cold ethereal suspension. With excess (3 mols.) of sulphuryl chloride, αα-*dichloroacetoacetanilide*, m. p. 46—47°, is formed, which tends to resinify on standing. By passing chlorine into an ethereal suspension of acetoacetanilide, a dark brown oil is produced which if dissolved in benzene slowly deposits crystals of αα-*dichloroacetoacet*-p-*chloroanilide* in very poor yield, m. p. 63—64°. α-Chloroacetoacetanilide is more stable than acetoacetanilide, being hydrolysed only by dilute hydrochloric acid at 120—130° to chloroacetone, carbon dioxide, and aniline.

β-n-*Butylaminocrotonanilide*, m. p. 98°, from *n*-butylamine and acetoacetanilide, is easily hydrolysed by water or dilute acids. By the interaction of α-chloroacetoacetanilide and alcoholic ammonia, α-*chloro*-β-*aminocrotonanilide*, m. p. 143°, is produced; it is stable on boiling with water, but is hydrolysed by dilute acids; α-*chloro*-β-*methylaminocrotonanilide*, m. p. 96·5°, is similar. α-*Chloro*-β-n-*butylaminocrotonanilide*, m. p. 65°, is very unstable. The interaction of aniline and α-chloroacetoacetanilide yields α : β-*diphenylaminocrotonanilide*, m. p. 201—202°.

β-*Chloro*-α-*hydroxylepidine*, m. p. 276°, is formed by treatment of α-chloroacetoacetanilide with concentrated sulphuric acid; the chlorine atom is very stable. On nitration, it gives a mononitro compound, probably 3-chloro-5-nitro-2-hydroxy-4-methylquinoline, m. p. above 330°.

By coupling α-chloroacetoacetanilide with diazotised aniline, *α-chloroglyoxylanilide phenylhydrazone*, NHPh·N:CCl·CO·NHPh, m. p. 161°, is produced. The chlorine is now easily replaceable, for with alcoholic ammonia, *α-aminoglyoxylanilide phenylhydrazone* is produced, m. p. 152—154°, apt to gelatinise. The *hydrochloride* is unstable, decomp. 150°; m. p. 213° in an atmosphere of dry hydrogen chloride. The corresponding *α-anilinoglyoxylanilide phenylhydrazone* has m. p. 171°. When chlorine is passed at 0° into an alcoholic suspension of α-chloroglyoxylanilide phenylhydrazone, the *2-chloroanilide* 2 : 4-*dichlorophenylhydrazone*, m. p. 199·5°, is formed; this was also synthesised from acetoacet-2-chloroanilide and 2 : 4-dichlorobenzenediazonium chloride.

α-Chloroglyoxylanilide o-*tolylhydrazone*, from the α-chloroacetoacetanilide and diazotised *o*-toluidine, has m. p. 115°; the p-*tolylhydrazone* has m. p. 175°; the 1 : 3 : 5-*xylylhydrazone*, m. p. 135·5°; the 1 : 3 : 4-*xylylhydrazone*, m. p. 138°. *α-Chloroglyoxylanilide phenylhydrazone*-o-*carboxylic acid*, from α-chloroacetoacetanilide and diazotised anthranilic acid, has m. p. 216—217° (decomp.). The β-*naphthylhydrazone* melts indistinctly at 183°, and the *α-naphthylhydrazone* at 189—191°. A. E. C.

***iso*Nitriles. VIII. Reaction with Aldehydes or Ketones in Presence of Organic Acids.** M. PASSERINI (*Gazzetta*, 1924, **54**, 529—540).—The reaction of an aldehyde or ketone with an aromatic *iso*nitrile in presence of an organic acid (cf. A., 1921, i, 895) is, with some exceptions, of general application and has now been extended to aliphatic aldehydes and to cases in which the aldehyde or ketone and the acid are derived from different organic radicals. Diketones also undergo this reaction, in which, however, only one of the two ketonic groups takes part. Neither camphor nor santonine reacts in this way. Halogenated ketones, which with water form hydrates, react with phenylcarbylamine in the same manner as the hydrates of halogenated aldehydes react in absence of organic acid (cf. A., 1922, i, 731).

α-Salicoyloxyisobutyranilide, $NHPh\cdot CO\cdot CMe_2\cdot O\cdot CO\cdot C_6H_4\cdot OH$, m. p. 118—119°, obtained from phenylcarbylamine, acetone, and salicylic acid, yields α-hydroxy*iso*butyranilide and salicylic acid on hydrolysis. *β-Chloro-α-benzoyloxyisobutyranilide*, $NHPh\cdot CO\cdot CMe(CH_2Cl)\cdot OBz$, from phenylcarbylamine, chloroacetone, and benzoic acid, m. p. 97—99°, yields α-hydroxy-β-chloro*iso*butyranilide and benzoic acid on hydrolysis.

β-Chloro-α-acetoxyisobutyranilide, $NHPh\cdot CO\cdot CMe(CH_2Cl)\cdot OAc$, from phenylcarbylamine, chloroacetone, and acetic acid, forms a pale yellow syrup and undergoes normal hydrolysis. *α-Acetoxy-α-methylbutyranilide*, NHPh·CO·CMeEt·OAc, m. p. 71°, from phenylcarbylamine, methyl ethyl ketone, and acetic acid, on hydrolysis yields acetic acid and *α-hydroxy-α-methylbutyranilide*, m. p. 114°, which undergoes further hydrolysis to aniline and α-hydroxy-α-methylbutyric acid. *α-Acetyl-lactanilide*, NHPh·CO·CHMe·OAc, m. p. 122°, from phenylcarbylamine, acetaldehyde, and acetic acid,

gives lactanilide on hydrolysis. *α-Benzoyl-α-benzoyloxy-α-phenylacetanilide*, NHPh·CO·CPhBz·OBz, from phenylcarbylamine, benzil, and acetic acid, m. p. 194—195° (decomp.), yields mandelanilide and benzoic acid on hydrolysis. m-*Nitro-α-benzoylmandelanilide*, NHPh·CO·CH(OBz)·C_6H_4·NO_2, m. p. 155—157°, from phenylcarbylamine, *m*-nitrobenzaldehyde, and benzoic acid, yields aniline, benzoic acid, and *m*-nitromandelic acid on hydrolysis.

o-*Benzoyl*-4 : 5-*dioxymethylenephenylglycollanilide*,

$$NHPh\cdot CO\cdot CH(OBz)\cdot C_6H_3<\begin{matrix}O\\O\end{matrix}>CH_2,$$

m. p. 160°, from phenylcarbylamine, piperonal, and benzoic acid, on hydrolysis, yields benzoic acid and 4 : 5-*dioxymethylenephenyl*-1-*glycollanilide*, m. p. 114°. ββ-*Dichloro-α-hydroxyisobutyranilide*, NHPh·CO·CMe(OH)·$CHCl_2$, m. p. 132—133°, from phenylcarbylamine and *as*.-dichloroacetone hydrate, yields aniline and ββ-dichloro-α-hydroxy*iso*butyric acid on hydrolysis. T. H. P.

Preparation of Sulphinanilides by Means of Grignard's Reaction. A. Sonn and E. Schmidt (*Ber.*, 1924, **57**, [*B*], 1355—1356).—*Benzenesulphinanilide*, Ph·SO·NHPh, m. p. 112—113°, *phenylmethanesulphinanilide*, m. p. 144—145°, and *ethanesulphinanilide*, m. p. 72°, are prepared from thionylaniline, PhN:S:O, and the requisite Grignard reagent in ethereal solution. H. W.

Amine Oxides derived from 4-Bromodimethylaniline and from 3- or 4-Nitrodimethylaniline. L. W. Jones and E. B. Hartshorn (*J. Amer. Chem. Soc.*, 1924, **46**, 1840—1855).—The various interpretations offered to explain the isomerides of $NMe_3(OMe)OH$ discovered by Meisenheimer (cf. A., 1913, i, 595, 1048), especially those of Jones and of Michael, and the more recent explanations of Lewis and Langmuir, are discussed. An attempt to prepare isomerides of the same type from oxides of substituted dimethylaniline was not successful since such amine oxides do not react with alkyl halides as methyl iodide reacts with trimethylamine oxide. Permonosulphuric acid oxidises the tertiary amines to the oxides, which crystallise from solution as neutral or acid sulphate. The corresponding hydrochlorides are stable, crystalline salts, but the hydriodides decompose, yielding free iodine and the original amine. *p*-Bromodimethylaniline oxide hydriodide was isolated below 0°. The free bases do not liberate iodine from potassium iodide, unlike the alkylpiperidine oxides (cf. Wernick and Wolffenstein, A., 1898, i, 536). Solutions of the free amine oxides were obtained by shaking the hydrochlorides in methyl alcohol with moist silver oxide. The solid bases were difficult to isolate, but were obtained in fair purity by removing the methyl alcohol rapidly under diminished pressure. Sublimation, even in a vacuum, causes decomposition, traces of formaldehyde being given off. The chief point of differentiation from the aliphatic amine oxides is in their behaviour with methyl iodide (cf. A., 1899, i, 682). No additive products with the amine oxide are formed, but the oxide is reduced and iodine liberated without the production of formaldehyde. An excess of iodine yields

periodides of the quaternary salts of the amines in most cases, *e.g.*, *m*-$NO_2 \cdot C_6H_4 \cdot NMe_3I \cdot I_2$. The following compounds were prepared: 4-*Bromodimethylaniline oxide*, brown, very hygroscopic powder, m. p. 167—168°, probably not pure; *sulphate*, $C_{16}H_{22}O_6Br_2N_2S$, darkens above 125° and explodes at 132—135°; *hydrochloride*, darkens above 160°, decomp. 165—166°; *hydriodide*, decomp. 92—94°; *picrate*, m. p. 126—127° (decomp.). 4-*Bromophenyltrimethylammonium iodide*, decomp. 187—187·5°, *periodide*, m. p. 165—166°. 4-*Nitrodimethylaniline oxide*, m. p. 110—111°, odour like coumarin; *hydrogen sulphate*, decomp. 147—149°; *hydrochloride*, decomp. 168—169°; *picrate*, m. p. 148—159°. Reduction of the hydrogen sulphate with sulphur dioxide gave mainly 4-nitrodimethylaniline, but also small amounts of what were assumed to be 5-nitro-2-dimethylaminobenzenesulphonic acid and 2-nitro-5-dimethylaminobenzenesulphonic acid. No quaternary salt was formed with methyl iodide; a small amount of a *periodide*, m. p. 162—163°, was separated from the main reduction product. 3-*Nitrodimethylaniline oxide*, m. p. 152—155°, has a slight odour of carbylamine; *hydrochloride*, decomp. 157—158°; *picrate*, m. p. 141—142°. m-*Nitrophenyltrimethylammonium iodide*, yellow prisms, decomp. about 200°; *periodide*, bronze plates, m. p. 144—145°.

A. C.

Catalytic Alkylation of Aniline. A. B. Brown and E. E. Reid (*J. Amer. Chem. Soc.*, 1924, **46**, 1836—1839).—Using silica gel as catalyst, a quantitative study of the alkylation of aniline by methyl, ethyl, *n*-propyl, and *n*-butyl alcohols has been made. The vapours of the mixture were passed over the catalyst at various temperatures (300—500°) until that at which the maximum conversion took place was found. The percentages of alkylanilines found and the ratios of monoalkyl to dialkyl at approximately optimum temperatures are as follows: series I for $NH_2Ph : ROH = 1 : 1{\cdot}05$, and series II, $1 : 2{\cdot}05$. Methyl, I 37·8%, 5 : 2 at 365°; II 42%, 5 : 3 at 370°. Ethyl, I 41·5%, 5 : 1 at 385°; II 60·0%, 7 : 2 at 385°. *n*-Propyl, I 38·8%, 14 : 3 at 385°; II 54·8%, 3 : 1 at 385°. *n*-Butyl, I 32·0%, 31 : 10 at 385°; II 40·3%, 33 : 10 at 400°. The catalyst was found to have a dehydrating and also a dehydrogenating effect on the alcohols, especially at higher temperatures, gaseous hydrocarbons of the C_nH_{2n} type being evolved together with hydrogen. The activity of the catalyst fell off rapidly in the first hour and then more slowly. This falling-off was not so marked if the catalyst was not heated to a high temperature. Fouling of the catalyst is to be expected owing to the formation of condensation products from aniline and aldehydes, which easily polymerise.

A. C.

***n*-Amylaniline.** L. G. Radcliffe and R. Grindley (*J. Soc. Dyers and Col.*, 1924, **40**, 290—292).—The preparation of *n*-butylaniline, *n*-amylaniline, and *n*-diamylaniline indicates that the reaction between aniline and an alkyl halide proceeds less smoothly and with much smaller yields as the molecular weight of the alkyl

halide is increased. A good yield of n-*amylaniline* was obtained by heating equimolecular proportions of aniline and *n*-amyl bromide or chloride under pressure at 190° for 6 hrs. The crude product was purified by fractional distillation, conversion into phenyl-*n*-amylnitrosoamine, and subsequent reduction by means of zinc dust and glacial acetic acid. n-*Amylaniline*, colourless oil, b. p. 260—262° (uncorr.), darkens when exposed to light. *Phenyl-n-amylnitrosoamine*, a greenish-yellow oil, slightly volatile in steam, decomposes when heated above 100°, and yields *p*-nitroso-*n*-amylaniline when treated with alcoholic hydrogen chloride. n-*Diamylaniline*, b. p. 280—285°, is produced by heating equimolecular proportions of *n*-amylaniline and *n*-amyl chloride under pressure at 190—200° for 2 hrs. Attempts to prepare the acetyl and benzoyl derivatives of *n*-amylaniline were unsuccessful. A. J. H.

Titanous Salts as Reducing Agents. E. Knecht (*J. Chem. Soc.*, 1924, **125**, 1537—1546).—If an acceptor, such as a primary aromatic amine, is present in solution, and the reactants are present in the ratio $2TiCl_3 : HNO_3$, titanous chloride will reduce nitric acid to nitrous acid; a quantitative yield of the diazonium compound can be obtained in this manner. When 1-nitronaphthalene is reduced with titanous chloride in presence of a large excess of hydrochloric acid, the principal product (94%) is 4-chloro-α-naphthylamine.

[With (Miss) E. Hibbert.]—Volumetric methods employing titanous chloride have been worked out for the determination of a number of organic compounds, including phenolphthalein, phenylhydrazine, tartrazine, tetramethyldiaminobenzhydrol, gallein, and isatin. S. B.

Oxidation of Didiphenylylamine. W. Bülow (*Ber.*, 1924, **57**, [*B*], 1431—1434).—Oxidation of didiphenylylamine, $NH(C_{12}H_9)_2$ (cf. Wieland and Süsser, A., 1911, i, 570), by sodium dichromate in the presence of glacial acetic acid and a little sulphuric acid, yields a dark green substance which is reduced by zinc dust to a substance, $C_{48}H_{36}N_2$, m. p. 276°, identical with the product obtained by Wieland and Süsser (*loc. cit.*) by the fission of tetradiphenylylhydrazine with ethereal hydrogen chloride; it is regarded as *o*-diphenylylaminotridiphenylylamine,

$$C_6H_3Ph(NH{\cdot}C_6H_4Ph)[N(C_6H_4Ph)_2].$$

In addition, diphenopiperazine, $C_6H_3Ph<\begin{matrix}N(C_6H_4Ph)\\N(C_6H_4Ph)\end{matrix}>C_6H_3Ph$, m. p. above 345°, is produced [Wieland and Süsser (*loc. cit.*) give m. p. 325—330°].

Tridiphenylylamine, m. p. 261—262°, is obtained together with the corresponding di-derivative from *p*-iododiphenyl and *p*-aminodiphenyl and copper powder (cf. Wieland and Süsser, *loc. cit.*). With antimony pentachloride, it yields a stable additive *compound*, $C_{36}H_{27}N,SbCl_5$, m. p. 130—131° (decomp.). H. W.

Steric Relations in the Acylation of Aromatic Amines and Aminophenols. L. C. Raiford, R. Taft, and H. P. Lankelma (*J. Amer. Chem. Soc.*, 1924, **46**, 2051—2057).—An

examination of the acetylation of thirteen substituted anilines by Sudborough's method (T., 1901, **79**, 533) indicates that the formation of a diacetyl derivative is favoured by the presence of one negative substituent (halogen or nitro) in the ortho-position to the amino group (cf. A., 1919, i, 12), and retarded by a similar substituent in the para-position. The accelerating effect is not in accordance with the relative weights of the substituents, and in the case of ortho-para substitution the two effects counterbalance. In the acylation of aminophenols with benzoyl chloride by the Schotten-Baumann process and with *p*-nitrobenzoyl chloride in pyridine or chloroform solution (cf. Fischer, A., 1920, i, 808), the presence of halogen atoms in the ortho-positions to the hydroxyl protects the hydroxyl group to a marked extent, but does not entirely prevent the formation of the *O*-acyl-*N*-acyl compound. With the symmetrical trihalogenated phenols steric hindrance is much more pronounced with benzoyl chloride than with *p*-nitrobenzoyl chloride, but only in the case of *s*-tribromoaniline was no acyl derivative obtained under these conditions. The following compounds were obtained: o-*Chlorodiacetanilide*, m. p. 86—87°; o-*iododiacetanilide*, m. p. 64—65°; 2 : 5-*dichlorodiacetanilide*, m. p. 91—92°; 2-*chloro*-4-*benzamidophenol*, m. p. 178°; 2-*chloro*-4-*benzamidophenyl benzoate*, m. p. 206°; 2-*chloro*-4-p-*nitrobenzamidophenol*, m. p. 242°; 2-*chloro*-4-p-*nitrobenzamidophenyl* p-*nitrobenzoate*, m. p. 253°; 2 : 6-*dichloro*-4-*benzamidophenol*, m. p. 198°; 2 : 6-*dichloro*-4-*benzamidophenyl benzoate*, m. p. 177°; 2 : 6-*dichloro*-4-p-*nitrobenzamidophenol*, m. p. 265°; 2 : 6-*dichloro*-4-p-*nitrobenzamidophenyl* p-*nitrobenzoate*, m. p. 246°; 2-bromo-4-benzamidophenol, m. p. 193° (cf. Meldola and Hollely, T., 1913, **103**, 182); 2-*bromo*-4-*benzamidophenyl benzoate*, m. p. 199°; 2-*bromo*-4-p-*nitrobenzamidophenol*, yellow needles, m. p. 237°; 2-*bromo*-4-p-*nitrobenzamidophenyl* p-*nitrobenzoate*, m. p. 255°; 2 : 6-*dibromo*-4-*benzamidophenol*, m. p. 208°; 2 : 6-*dibromo*-4-*benzamidophenyl benzoate*, m. p. 172°; 2 : 6-*dibromo*-4-*p-nitrobenzamidophenol*, m. p. 268°; 2 : 6-*dibromo*-4-p-*nitrobenzamidophenyl* p-*nitrobenzoate*, m. p. 237°; 2 : 6-di-iodo-4-nitrophenol, m. p. 155—156° (cf. Weselsky, *Annalen*, 1874, **174**, 108; Post, *ibid.*, 1880, **205**, 91); 2 : 6-di-iodo-4-aminophenol, m. p. 169—171° (cf. Seifert, *J. pr. Chem.*, 1843, [ii], **28**, 437); 2 : 6-*di-iodo*-4-*benzamidophenol*, m. p. 222°; 2 : 6-*di-iodo*-4-*benzamidophenyl benzoate*, m. p. 210—211°; 2 : 6-*di-iodo*-4-p-*nitrobenzamidophenyl* p-*nitrobenzoate*, m. p. 277°; 2 : 4 : 6-*trichlorophenyl benzoate*, m. p. 74°; 2 : 4 : 6-*trichlorophenyl* p-*nitrobenzoate*, m. p. 105—106°; 2 : 4 : 6-*tribromophenyl benzoate*, m. p. 81°; 2 : 4 : 6-*tribromophenyl* p-*nitrobenzoate*, m. p. 153—154°; 2 : 4 : 6-*tri-iodophenyl* p-*nitrobenzoate*, m. p. 181°; *phenyl* p-*nitrobenzoate*, m. p. 129°, and 2-*nitrobenzanilide*, m. p. 212°. R. B.

Mutual Solubility. III. Mutual Solubility of Glycerol and Amino and Hydroxy Compounds. R. R. PARVATIKER and B. C. MCEWEN.—(See ii, 659.)

Aromatic Orthoformates. J. E. DRIVER (*J. Amer. Chem. Soc.*, 1924, **46**, 2090—2093).—The method recently described for

the preparation of triphenyl orthoformate (this vol., i, 638) can be used for the preparation of the tolyl orthoformates. The action of chloroform vapour on potassium *p*-tolyloxide at 108° gives tri-*p*-tolyl orthoformate, m. p. 112° (Auwers, A., 1907, i, 400), and traces of 1-methyl-1-dichloromethyl-$\Delta^{2:5}$-*cyclo*hexadien-4-one, m. p. 53—55°, the formation of the latter compound suggesting that an unstable dichloromethoxytoluene is the first product of the reaction. Similarly, potassium *o*-tolyloxide and boiling chloroform give *tri*-o-*tolyl orthoformate*, m. p. 96°, and potassium *m*-tolyloxide at 110—120° yields *tri*-m-*tolyl orthoformate*, m. p. 50°. The tolyl orthoformates are not hydrolysed by boiling alkalis and are only slowly oxidised by boiling neutral permanganate. R. B.

Decomposition of Ethers by Metallic Sodium. II. Relative Tenacity of Different Radicals to the Oxygen Atom. P. Schorigin (*Ber.*, 1924, **57**, [*B*], 1627—1634; cf. A., 1923, i, 207).—The decomposition of mixed ethers, particularly those of the aromatic and fatty-aromatic series, by sodium occurs in accordance with the scheme: $R{\cdot}O{\cdot}R^1+2Na \rightarrow RR^1O{\cdots}Na_2 \rightarrow R{\cdot}ONa+R^1Na$ or $R{\cdot}Na+R^1{\cdot}ONa$. The reaction has been applied to the determination of the relative firmness with which the radicals are attached to the oxygen atom. As is to be expected, the reaction takes place in both possible directions, but the more firmly bound of any two radicals is found to the greater extent as alkoxide or phenoxide in the products. The groups may be arranged in order of increasing tenacity to oxygen in the order: benzyl, ethyl, *iso*amyl, β-naphthyl, α-naphthyl, phenyl. The relative positions of the naphthyl groups in the series is slightly uncertain.

Phenyl α-naphthyl ether and sodium at 140° give a mixture of phenol and α-naphthol (molecular ratio, 5 : 1) and benzene and naphthalene (1 : 10) The corresponding ratios for phenyl β-naphthyl ether are 7 : 1 and 1 : 8. αβ-Dinaphthyl ether did not give a definite result by reason of the difficulty of separating α- from β-naphthol. β-Naphthyl ethyl ether yielded β-naphthol and ethyl alcohol (4 : 1) and naphthalene, ethane, and ethylene (1 : 3·3). β-Naphthyl benzyl ether gave only β-naphthol and toluene. Phenyl benzyl ether yielded only phenol and toluene with traces of benzene; it is isomerised to some extent to benzhydrol (cf. Schorigin, this vol., i, 1188). Phenetole gave almost exclusively phenol accompanied by a very little ethyl alcohol; ethane and ethylene are produced, but, apparently, no benzene. Benzyl ethyl ether gave an inseparable mixture of little benzyl alcohol and much phenylethylcarbinol, toluene, and ethylene. Diethyl ether is decomposed by sodium at 200—340° into ethylene, probably ethane and hydrogen, and a little ethyl alcohol. Di*iso*amyl ether is decomposed with greater difficulty than the diethyl compound, yielding β-methyl-Δ^{α}-butylene, β-methyl-Δ^{β}-butylene, and *iso*-pentane. H. W.

Superheating of Uniform Organic Compounds. I. Aryl-paraffins and Aliphatic Esters. S. Skraup and F. Nieten (*Ber.*, 1924, **57**, [*B*], 1294—1310).—The pyrogenic decomposition

of anisylparaffins in sealed tubes at as low a temperature as possible leads, in the case of compounds with an even number of carbon atoms in the aliphatic chain, to the loss of the terminal methyl group (as ethylene) and production of the next lower homologue with an odd number of carbon atoms. Under similar conditions, the compounds with an odd number of carbon atoms remain unchanged, but at a slightly higher temperature they lose the complete aliphatic chain, probably as olefine, and yield anisole. The phenyl esters of stearic and palmitic acids decompose at 300—320° in sealed tubes filled with nitrogen into pentadecane and tridecane, respectively, and phenyl acrylate; the latter is converted primarily into acetylene and phenyl formate, which then yields phenol and carbon monoxide. In an open vessel, on the other hand, phenyl stearate is decomposed at 320° into carbon monoxide, possibly hydrogen and phenol; acetylene, ethylene, or paraffin hydrocarbons are not produced, the chief product being a carbonised residue.

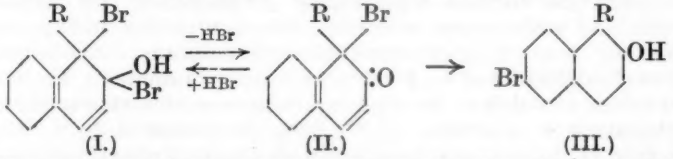
p-*Anisyl* n-*propyl ketone*, b. p. 162—163°/20 mm., m. p. −3° to −4° (*phenylhydrazone*, m. p. 77°), is prepared by the action of aluminium chloride on a solution of anisole and butyryl chloride in light petroleum or by the action of butyryl chloride on *p*-anisylchloromercurate at 135°. If light petroleum is replaced by carbon disulphide, the yield of the ketone is decreased and the product contaminated with αα-*di*-p-*anisyl*-Δ^{α}-*butylene*, $CHEt{:}C(C_6H_4{\cdot}OMe)_2$, m. p. 95—96°. The ketone is reduced by amalgamated zinc and hydrochloric acid to *p*-butylanisole (*sulphonamide*, m. p. 96°). p-*Anisyl* n-*butyl ketone*, b. p. 165—167°/14 mm., m. p. 26° (*phenylhydrazone*, m. p. 73°), is converted similarly into p-n-*amylanisole*, b. p. 124—125°/14 mm. (*sulphonamide*, m. p. 101°). p-*Anisyl* n-*amyl ketone*, m. p. 41° (*phenylhydrazone*, m. p. 28°), p-*hexylanisole*, b. p. 152—153°/15 mm., and its *sulphonic acid*, m. p. 75°, and *sulphonamide*, m. p. 87°, are described. p-*Anisyl* n-*hexyl ketone*, b. p. 192°/17 mm., m. p. 40° (*phenylhydrazone*, m. p. 35°), gives p-*heptylanisole*, b. p. 160—162°/17 mm. (*sulphonamide*, m. p. 108°). p-*Anisyl* n-*octyl ketone*, m. p. 43° (*phenylhydrazone*, m. p. 48°), yields p-*nonylanisole*, b. p. 178—180°/18 mm.

Phenyl β-chloropropionate, b. p. 141—143°/18 mm., is converted by boiling pyridine into *phenyl acrylate*, b. p. 202—203° (slight decomp.), 105°/20 mm., and, apparently, the quaternary *compound*, $C_5H_5NCl{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et$, which, however, is not an intermediate product in the formation of the acrylate.

The action of propionyl chloride on dimethylaniline in the presence of zinc chloride gives a mixture of αα-*bisdimethylaminophenyl*-Δ^{α}-*propylene* (the constitution of which is established by its oxidation to Michler's ketone) and p-*dimethylaminopropiophenone*, b. p. 270—272° (phenylhydrazone, m. p. 58°); the ketone is also prepared from propionyl chloride and dimethylaminophenylchloromercurate. Similarly, dimethylaniline, butyryl chloride, and zinc chloride yield p-*dimethylaminophenyl* n-*propyl ketone*, b. p. 180—185°/27 mm. (*phenylhydrazone*, m. p. 67—68°; *methiodide*, m. p. 163°), which does not appear to undergo reduction by Clem-

mensen's method, and *αα-bisdimethylaminophenyl-Δ$^{\alpha}$-butylene*, m. p. 80—81°, which is oxidised to Michler's ketone. H. W.

Reaction Processes Underlying Substitution. K. FRIES and H. ENGEL (*Annalen*, 1924, **439**, 232—245).—By the bromination of derivatives of β-naphthol, under definite conditions, the intermediate products are ketobromides, derivatives of 1 : 2-dihydronaphthalene. The bromination is carried out in the cold in acetic acid in presence of sodium acetate; otherwise the products are insoluble resins. By the further action of hydrogen bromide or chloride in acetic acid, the product isomerises, giving the corresponding 6-bromo-β-naphthol, the rate of isomerisation depending on the concentration of the halogen acid; the change takes place more rapidly with hydrogen bromide than with hydrogen chloride, and in the latter case no 6-chloro-β-naphthol is formed. The first step in the bromination is supposed to consist in the addition of two atoms of bromine to the 1 : 2-double bond I followed by loss of hydrogen bromide to give the bromoketone II, which in its turn is more or less easily isomerised to III. [R=Br, Me, Et.]



(I.) (II.) (III.)

1-Bromo-β-naphthol on bromination under the above conditions yields 1 : 1-*dibromo*-2-*keto*-1 : 2-*dihydronaphthalene*, m. p. 70°, unstable in light or on warming. Reduction with zinc and acetic acid regenerates the bromonaphthol, and by treatment with hydrogen bromide or chloride in acetic acid, 1 : 6-dibromo-β-naphthol is produced. By further bromination of the ketobromide, 1 : 1 : 6-*tribromo*-2-*keto*-1 : 2-*dihydronaphthalene*, m. p. 115°, is produced, which on reduction yields 1 : 6-dibromo-β-naphthol. The tribromo-compound is stable to hydrogen bromide in acetic acid at the ordinary temperature.

1-*Bromo*-2-*keto*-1-*methyl*-1 : 2-*dihydronaphthalene*, m. p. 80°, which is stable to dilute alkali, on reduction yields 1-methyl-β-naphthol. With silver acetate in acetic acid, the ketobromide yields 1-*acetoxy*-2-*keto*-1-*methyl*-1 : 2-*dihydronaphthalene*, and by the action of halogen acids as above, it isomerises to 6-bromo-1-methyl-β-naphthol, which forms a molecular compound with its acetyl derivative, $C_{11}H_9OBr{\cdot}C_{13}H_{11}O_2Br$, m. p. 119°. 6-*Bromo*-1-*methyl*-β-*naphthol* on bromination yields 1 : 6-*dibromo*-2-*keto*-1-*methyl*-1 : 2-*dihydronaphthalene*, yellow prisms.

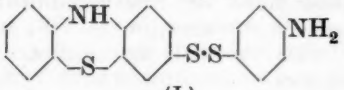
1-*Ethyl*-β-*naphthol*, m. p. 105°, was obtained from 1-acetyl-β-naphthol by Clemmensen's reduction method. It is unstable in the air. The *acetyl* derivative melts at 53°. On bromination in acetic acid in the absence of sodium acetate, 6-*bromo*-1-*ethyl*-β-*naphthol* is formed, m. p. 109°; *acetyl* derivative, m. p. 138°. By bromination in presence of sodium acetate, the product is 1-*bromo*-2-*keto*-1-*ethyl*-1 : 2-*dihydronaphthalene*, m. p. 71°. By the

action of hydrogen bromide in acetic acid solution, a mixture of 6-*bromo*-1-*ethyl*-β-*naphthol* and its *acetyl* derivative is formed, the proportions depending on the concentration of the halogen acid. 1 : 6-*Dibromo*-2-*keto*-1-*ethyl*-1 : 2-*dihydronaphthalene*, m. p. 103°, on reduction gives 6-bromo-1-ethyl-β-naphthol. By the action of sodium nitrite and acetic acid on the ethereal solution of the last-named compound, 6-*bromo*-1-*nitro*-2-*keto*-1-*ethyl*-1 : 2-*dihydronaphthalene* is obtained, m. p. 112°, unstable on warming. A. E. C.

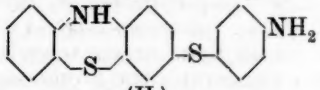
Action of Oxalyl Chloride on Naphthols. M. Giua and V. de Franciscis.—(See i, 1092.)

Ultra-violet Absorption Spectra of some Derivatives of Naphthols. S. Komatsu, B. Masumoto, and S. Kumamoto.—(See ii, 642.)

Direct Sulphuration of Aniline. H. H. Hodgson (*J. Chem. Soc.*, 1924, **125**, 1855—1858).—The initial product of the action of sulphur on aniline at 170—180° is 2 : 2′-diaminodiphenyl disulphide, but increasing quantities of 4 : 4′-diaminodiphenyl disulphide are formed with rising temperature. On prolonged heating and with excess of aniline, the disulphides undergo transformation into 2 : 2′-diaminodiphenyl sulphide, 2 : 4′-diaminodiphenyl sulphide, and 4 : 4′-diaminodiphenyl sulphide. On heating with excess of sulphur, by diphenylamine condensation and further sulphuration a *substance*, $C_{18}H_{14}N_2S_3$, is produced to which the structure (I) is assigned, together with its desulphuration product,



(I.)



(II.)

$C_{18}H_{14}N_2S_2$ (II). The latter yields a brilliant red pigment when diazotised and coupled with β-naphthol. The azo-β-naphthol derivative of 4 : 4′-diaminodiphenyl disulphide is described. Merz and Weith's thioaniline from sulphur and boiling aniline (*Ber.*, 1871, **4**, 384) is 2 : 4′-diaminodiphenyl sulphide with a little 4 : 4′-diaminodiphenyl sulphide; their product in the presence of lead oxide is the latter sulphide (cf. Nietzki and Bothof, A., 1895, i, 132). Lead oxide thus promotes para-substitution (cf. Hodgson and Dix, T., 1914, **105**, 952). R. B.

Mechanism of Aniline Thionation [Sulphuration] with Observations on the Therapeutical Importance of the Dithioanilines. H. H. Hodgson (*J. Soc. Dyers and Col.*, 1924, **40**, 330—337).—A restatement of results already reported (preceding abstract). W. A. S.

Transformation of Benzyl Ethers into Carbinols. I. P. Schorigin (*Ber.*, 1924, **57**, [*B*], 1634—1637).—The action of sodium on phenyl benzyl ether at 100° (cf. Schorigin, i, 1185), leads to the production of benzhydrol in 30—35% yield. Benzyl ethyl ether and β-naphthyl benzyl ether similarly give phenylethylcarbinol and phenyl-β-naphthylcarbinol. The presence of the

benzyl group in the ether appears to be essential for the transformation, $CH_2Ph{\cdot}O{\cdot}R \longrightarrow CHPh(OH){\cdot}R$. H. W.

Preparation of Alcohols from Aldehydes. BADISCHE ANILIN- UND SODA-FABRIK (D.R.-P. 384351; from *Chem. Zentr.*, 1924, i, 2398).—Alcohols are prepared from aldehydes by reduction with hydrogen in the presence of activated magnesium. Examples are given of the preparation of cinnamyl alcohol, geraniol, b. p. 114—116°/13 mm., citronellol, b. p. 117—119°/17 mm., β-phenylpropyl alcohol, b. p. 104—106°/10 mm., heptyl alcohol, b. p. 78—80°/12·5 mm., phenylethyl alcohol, and benzyl alcohol from the corresponding aldehydes. G. W. R.

Intramolecular Change. Identification of the Products of Dehydration of αα*γ*-Triphenyl-ββ-dimethylpropan-α-ol. (MME.) P. RAMART (*Compt. rend.*, 1924, **179**, 400—402).—Magnesium benzyl chloride condenses readily with αα-diphenylethyl methyl ketone (ββ-diphenylbutan-γ-one) giving *αα*γ-triphenyl-β-methylbutan-β-ol*, $CPh_2Me{\cdot}C(OH)Me{\cdot}CH_2Ph$, m. p. 78—80°, b. p. 225—230°/3 mm., which on dehydration with a mixture of acetyl chloride and acetic anhydride, or by warming with infusorial earth, yields a mixture of two hydrocarbons, m. p. 110° and 90° respectively, which are identical with those previously obtained by the dehydration of αα*γ*-triphenyl-ββ-dimethylpropan-α-ol (this vol., i, 1062). The two hydrocarbons are regarded as stereoisomeric forms of αα*γ*-triphenyl-β-methyl-Δ$^{\gamma}$-butene, $CPh_2Me{\cdot}CMe{:}CHPh$. Their formation from αα*γ*-triphenyl-ββ-dimethylpropan-α-ol involves an intramolecular change prior to dehydration:

$$CPh_2(OH){\cdot}CMe_2{\cdot}CH_2Ph \longrightarrow CPh_2Me{\cdot}C(OH)Me{\cdot}CH_2Ph.$$

The possibility of the alternative change

$$CPh_2(OH){\cdot}CMe_2{\cdot}CH_2Ph \longrightarrow CH_2Ph{\cdot}CPh_2{\cdot}CMe_2{\cdot}OH$$

is excluded, since the *γγδ-triphenyl-β-methylbutan-β-ol*, b. p. 205—210°/1 mm., obtained in 80—100% of the theoretical yield from magnesium methyl iodide and benzyl diphenylbenzylacetate, is dehydrated with difficulty, even by phosphoric anhydride, yielding a mixture of unchanged alcohol and a *hydrocarbon*, $C_{23}H_{22}$, b. p. 196—199°/3 mm., 235—236°/25 mm., which does not take up bromine. R. B.

Transformation of Cinnamaldehyde into Cinnamyl Alcohol, and the Constitution of Cubebin. H. PAULY, H. SCHMIDT, and E. BÖHME (*Ber.*, 1924, **57**, [*B*], 1327—1330).—The reduction of cinnamaldehyde diacetate by iron and acetic acid (Barbier and Léser, A., 1905, i, 653) depends essentially on the action of ferrous acetate on cinnamaldehyde whereby cinnamyl alcohol (diphenylurethane, m. p. 98°; *phenylurethane*, m. p. 91—91·5°) is produced. γ-Hydroxy-αζ-diphenylhexane, b. p. 130—136°/2 mm. (cf. von Braun and Kochendörfer, A., 1923, i, 1197), is formed as by-product together with resinous material. Piperonylacraldehyde is reduced in a similar manner to *β-piperonylallyl alcohol*, m. p. 123°. This substance is not identical with cubebin, to which its structure has been assigned (cf. Mameli, A., 1922, i, 347). Cinnamaldehyde

cannot be converted into cinnamyl alcohol and cinnamic acid by Cannizzaro's reaction to an extent greater than 10%. H. W.

Benzeins. III. R. MEYER and E. FUNKE (*Ber.*, 1924, **57**, [*B*], 1360—1363).—Schroeter's "dihydroxydimethyltriphenylcarbinol," prepared by the action of benzotrichloride on *o*-cresol, loses a molecular proportion of water when heated at 140—150°, and is therefore to be regarded as *o*-cresolbenzein,

$$C_6H_3Me(OH)\cdot CPh{:}C_6H_3Me{:}O,H_2O.$$

It is conveniently purified through the *hydrochloride*. The *dibenzoate*, m. p. 134°, is described. Addition of hydrogen cyanide to *o*-cresolbenzein yields the colourless *cyanohydrin*,

$$CN\cdot CPh[C_6H_3Me(OH)]_2,$$

m. p. 147°, which is converted by benzoyl chloride in the presence of sodium hydroxide into *dibenzoxydimethyltriphenylmethanecarboxylamide*, $NH_2\cdot CO\cdot CPh(C_6H_3Me\cdot OBz)_2$, m. p. 56°. *o*-Cresolbenzein is transformed by an excess of bromine in glacial acetic acid solution into *dibromo-o-cresolbenzein*, $C_6H_2BrMe(OH)\cdot CPh{:}C_6H_2BrMe{:}O,H_2O$, which loses a molecular proportion of water at 140°; it yields a blue *sodium* salt, $C_{21}H_{15}O_2Br_2Na,H_2O$.

Dihydroxydimethyltriphenylmethane, m. p. 170°, is prepared by the condensation of benzaldehyde with *o*-cresol in the presence of sulphuric acid. H. W.

Sulphonefluorescein and Dihydroxybenzoylbenzene-*o*-sulphonic Acid, and some of their Derivatives. W. R. ORNDORFF and R. S. VOSE (*J. Amer. Chem. Soc.*, 1924, **46**, 1896—1912).—Sulphonefluorescein has only been obtained previously in the amorphous condition and of doubtful purity. Five different methods of preparation are described. Heating resorcinol with "saccharin" and sulphuric acid at 135—140° gives a 52% yield, whilst *o*-sulphobenzoyl chloride with resorcinol at 100° gives 41% of the theoretical yield. Contrary to Fahlberg and Barge and to White (A., 1896, i, 49; 1889, 709), it is obtained on heating *o*-sulphobenzoic anhydride with resorcinol at 135—140°, the reaction taking place in two stages with formation of *o*-2 : 4-dihydroxybenzoylbenzenesulphonic acid as intermediate product. Sulphonefluorescein separates in red needles with a blue surface colour which causes them to appear purple. When finely divided (rapid precipitation or grinding) it is bright yellow. Similarly prepared alkaline solutions of sulphonefluorescein and ordinary fluorescein are indistinguishable by the unaided eye, although the fluorescence of sulphonefluorescein is 10% more intense than that of fluorescein. In both cases the fluorescence spectrum consists of a single band extending approximately from λ 5000 to λ 5900, with a maximum at λ 5249 for sulphonefluorescein and at λ 5209 for fluorescein. Sulphonefluorescein gives rise to coloured quinonoid and colourless lactoid derivatives. Sulphonefluorescein itself does not occur in the lactoid form, but is probably a solid solution of the quinonoid form (as an oxonium or carbonium salt) and the quinonoid hydrate. It acts as a monobasic acid and forms highly coloured salts, soluble

in water with a green fluorescence: the *ammonium* salt is a dark red powder containing $2H_2O$; *barium* salt, and *zinc* salt ($7H_2O$), orange crystals. On reduction with zinc dust in water sulphonefluorescein is converted into the *zinc* salt of *sulphonefluorescin*, a nearly colourless solid which becomes yellow in air and on heating in air at 120—125° is changed to the orange-red salt of the fluorescein. *Sulphonefluorescin* forms straw-coloured crystals when isolated from the zinc salt. It is extremely soluble in water (in contrast to the unreduced substance). The solution in sodium hydroxide is colourless and almost non-fluorescent, but marked fluorescence appears on standing. *Sulphonefluorescin diacetate* has m. p. 230° (decomp.). Exposed to dry ammonia, sulphonefluorescein takes up 4 mols., 3 of which are lost on exposure to concentrated sulphuric acid. A *dianilino* compound, green crystals which do not melt at 320°, probably an inner ammonium salt, is formed on boiling sulphonefluorescein with aniline. *Sulphonefluorescein monoacetate*, dark green crystals, decomp. without melting above 300°, and the *monobenzoate*, yellow crystals, which dissolve in sodium hydroxide to deep purple solution, have the quinonoid structure; the *diacetate*, orange-yellow crystals, decomp. 209°, has the lactoid structure. Sulphonefluorescein reacts both with benzoyl chloride and phosphorus pentachloride to form the same *dichloride*, colourless, decomp. 320°, in which the chlorine atoms have replaced the hydroxyl groups. This forms a disodium (coloured) and a trisodium salt (colourless), and a *hydrate*, $C_{19}H_{10}O_4Cl_2S,H_2O$, red, orange to greenish-orange by transmitted light. *Dibromosulphonefluorescein*, red needles with silky lustre, not melting at 300°, is soluble in dilute alkali forming solutions intensely green by reflected light and orange to red by transmitted light. The tetrabromo compound described by Sisley could not be made. The *diacetate*, which does not melt at 300°, is hydrolysed by water. It absorbs 4 mols. of ammonia and loses 3 of them over concentrated sulphuric acid. *Di-iodosulphonefluorescein*, red needles, forms a *diacetate*, short, yellow prisms, dark red at 315°. *o*-2 : 4-Dihydroxybenzoylbenzenesulphonic acid, prepared from the ammonium salt (containing $3H_2O$), behaves as a monobasic acid towards methyl-red, but as dibasic to phenolphthalein. The 3 : 5-*dibromo* derivative, m. p. 110—112°, contains $2{\cdot}5H_2O$. It titrates as a dibasic acid with both of the above indicators. A. C.

Simple Synthesis of the Salts of *N*-Benzylideneamino-acids. O. Gerngross and E. Zühlke (*Ber.*, 1924, **57**, [*B*], 1482—1489).—The sodium salts of arylideneamino-acids are obtained in almost quantitative yield by the action of an alcoholic solution of sodium ethoxide on an alcoholic solution of the ester of the amino-acid and the requisite aldehyde. Hydrolysis is ascribed to the action of sodium hydroxide formed from the ethoxide and water liberated by the partial condensation of the aldehyde and ester. The separation of the sodium salt disturbs the equilibrium established otherwise between amino ester, aldehyde, and arylideneamino ester and thus causes the completion of the reaction. The arylidene deriv-

atives are very stable towards alkali hydroxide, but are hydrolysed with great ease by acids.

Ethyl p-*nitrobenzylideneaminoacetate*, $NO_2 \cdot C_6H_4 \cdot CH:N \cdot CH_2 \cdot CO_2Et$, m. p. 148°, is readily prepared from ethyl aminoacetate and benzaldehyde in alcoholic solution. *Methyl* l-α-p-*nitrobenzylideneamino*-β-*hydroxyphenylpropionate*, m. p. 125°, is obtained similarly.

Sodium benzylideneaminoacetate, decomp. 255—260°, results from the action of sodium ethoxide on ethyl aminoacetate and benzaldehyde in alcoholic solution; the *copper*, *calcium*, and *silver* salts are described. *Sodium* α-*benzylideneaminopropionate*, *sodium* l-α-*benzylideneamino*-β-*hydroxyphenylpropionate*, decomp. 275° after darkening at 240°, and the hygroscopic sodium salt of benzylideneglycylglycine are similarly prepared.

[With J. Rothe.]—*Sodium piperonylideneaminoacetate*, m. p. 232°, is prepared from glycine ester hydrochloride, sodium ethoxide, and piperonal.

[With J. Jodé.]—Contrary to the observations of Puxeddu (A., 1909, i, 720), 5-*o*-nitrobenzylideneaminosalicylic acid is rather more resistant than the corresponding derivatives of aliphatic acids towards hydrochloric acid, but is smoothly hydrolysed by the mineral acid at varying concentrations into its components without giving indications of the formation of a hydrochloride. H. W.

Action of Triphenylmethyl Chloride on Ethyl β-Aminocrotonate and Analogous Compounds. E. Benary and P. Lorth (*Ber.*, 1924, **57**, [*B*], 1324—1327).—Triphenylmethyl chloride resembles acyl chlorides (A., 1923, i, 37, and previous abstracts) in its ability to react with β-aminocrotonic esters and related substances. It appears generally to yield only *N*-derivatives and to react only with compounds containing the unsubstituted amino group.

Ethyl β-aminocrotonate is converted by triphenylmethyl chloride in the presence of pyridine at 100° into *ethyl* β-*triphenylmethylaminocrotonate*, $CH_3 \cdot C(NH \cdot CPh_3):CH \cdot CO_2Et$, m. p. 137—138°, which is inactive towards phenylhydrazine and is converted by alcoholic potassium hydroxide solution into *acetonetriphenylmethylimide*, $CMe_2:N \cdot CPh_3$, m. p. 162° (*tribromide*, m. p. 235° after darkening at 230°). β-*Triphenylmethylaminocrotononanilide*, m. p. 209°, β-*triphenylmethylaminocrotononitrile*, m. p. 250—251°, N-*triphenylmethylbenzoacetodinitrile*, $CPh_3 \cdot NH \cdot CPh:CH \cdot CN$, m. p. 228—229°, N-*triphenylmethylacetylacetoneamine*, $CHAc:CMe \cdot NH \cdot CPh_3$, m. p. 161°, and N-*triphenylmethylbenzoylacetoneamine*, $CHBz:CMe \cdot NH \cdot CPh_3$, m. p. 192—193°, are prepared similarly. H. W.

Preparation of Anilides and Esters. E. de B. Barnett and I. G. Nixon (*Chem. News*, 1924, **129**, 190—191).—Excellent yields of anilides and esters are obtained by slowly adding thionyl chloride (1 mol.) to a well-cooled equimolecular solution of the acid and phenol or primary amine in pyridine, the mixture being poured into water after 1 hour at the ordinary temperature. Phenylacetic acid gives very poor results, and the method fails with

diphenylamine and 1-aminoanthraquinone; with aliphatic alcohols, the results are uncertain. The following corrected m. p. are given: *iso*eugenyl benzoate, 106°; β-naphthyl *p*-nitrobenzoate, 169°; *o*-nitrophenyl *m*-nitrobenzoate, 129°; *m*-tolyl *p*-nitrobenzoate, 90°; *p*-nitrobenzanilide, 216°; *p*-nitrobenzo-*p*-nitroanilide, 274°; *p*-nitrobenzo-*o*-nitroanilide, 277°. The following compounds are new: o-*nitrophenyl* o-*nitrobenzoate*, m. p. 125°; o-*nitrophenyl anisate*, m. p. 96°; p-*nitrophenyl* o-*nitrobenzoate*, m. p. 111°; p-*nitrophenyl* p-*nitrobenzoate*, m. p. 159°; p-*nitrophenyl anisate*, m. p. 166°; p-*nitrophenyl* 3 : 5-*dinitrobenzoate* (+1 mol. acetic acid), m. p. 188°; *pyrocatechyl di*-p-*nitrobenzoate*, m. p. 169°; *quinyl di*-p-*nitrobenzoate*, m. p. 258°; β-*naphthyl* o-*nitrobenzoate*, m. p. 112°; β-*naphthyl* m-*nitrobenzoate*, m. p. 134°. R. B.

Pressor Anæsthetics. I. C. S. MARVEL and V. DU VIGNEAUD (*J. Amer. Chem. Soc.*, 1924, **46**, 2093—2099).—Three compounds have been prepared which contain both the grouping Ph·C·C·N< characteristic of pressor activity (Barger and Dale, A., 1910, ii, 984) and Ph·CO·O·C·C·NR_2, characteristic of local anæsthetic power (Pyman, T., 1908, **93**, 1796; 1917, **111**, 1121). Two of the compounds, 2-diethylamino-1-hydrindyl *p*-aminobenzoate hydrochloride and 2-di-*n*-butylamino-1-hydrindyl *p*-aminobenzoate hydrochloride, have only a very slight anæsthetic action, that of the diethylamino compound being the greater, whilst the third compound, α-phenyl-β-diethylaminoethyl *p*-aminobenzoate hydrochloride (phenylprocaine), has a strong anæsthetic action and a low toxicity. None of these three compounds showed any appreciable pressor action, and there is no record of the pressor activity of a similar compound containing both linkings, CH_2O_2·C_6H_3·CH(CO_2Ph)·CH_2·NMe_2 (Pyman, T., 1908, **93**, 1796), or of the benzoyl esters of ethyl- and diethyl-mydriatine.

2-Bromo-1-hydroxyhydrindene (Pope and Read, T., 1912, **101**, 762) readily condenses with *p*-nitrobenzoyl chloride in benzene solution in the presence of pyridine, giving 2-*bromo*-1-*hydrindyl* p-*nitrobenzoate*, m. p. 131°, which could not be condensed with diethylamine. Diethylamine and 2-bromo-1-hydroxyhydrindene readily give 2-*diethylamino*-1-*hydroxyhydrindene*, b. p. 165—167°/15 mm., d^{20} 1·043, n_D^{20} 1·5393, which readily turns red in the air, in 56—60% yield (*hydrochloride*, m. p. 175°); it condenses with *p*-nitrobenzoyl chloride in the presence of pyridine giving (yield 50—59%) 2-*diethylamino*-1-*hydrindyl* p-*nitrobenzoate*, yellow crystals, m. p. 85°. The *hydrochloride*, m. p. 210—212°, is obtained by condensing in the absence of pyridine, and on reduction with iron yields 2-*diethylamino*-1-*hydrindyl* p-*aminobenzoate hydrochloride*, m. p. 206° (yield 48%). Similarly, di-*n*-butylamine and 2-bromo-1-hydroxyhydrindene in benzene solution give in 63—65% yield, 2-*di*-n-*butylamino*-1-*hydroxyhydrindene*, rapidly turning red, b. p. 155—165°/7 mm., n_D^{20} 1·493, which with *p*-nitrobenzoyl chloride in benzene solution gives, in 60—67% yield, 2-*di*-n-*butylamino*-1-*hydrindyl* p-*nitrobenzoate hydrochloride*, m. p. 155—156°. Reduction of the hydrochloride with iron in neutral solution gives, in 72—

85% yield, 2-*di*-n-*butylamino*-1-*hydrindyl* p-*aminobenzoate*, m. p. 74° (*hydrochloride*, m. p. 229—230°, *hydrogen sulphate*, m. p. 200—201°). ω-Chloroacetophenone and diethylamine in benzene solution yield *ω-diethylaminoacetophenone*, b. p. 148—152°, n_D^{25} 1·5180, which on reduction by Adams and Voorhees' method (A., 1922, ii, 558) yields *α-phenyl-β-diethylaminoethyl alcohol*, n_D^{25} 1·507, and this with *p*-nitrobenzoyl chloride in benzene solution gives (yield 89—91%) *α-phenyl-β-diethylaminoethyl* p-*nitrobenzoate hydrochloride*, m. p. 155—156° (*nitrate*, m. p. 161·5°, insoluble in water) from which by reduction with iron at 45—50° is obtained *α-phenyl-β-diethylaminoethyl* p-*aminobenzoate*, m. p. 88—89° (*hydrochloride*, m. p. 210—212°). R. B.

Preparation of Acid Anhydrides. E. DE B. BARNETT and J. W. COOK (*Chem. News*, 1924, **129**, 191).—Acid anhydrides may be obtained in about 70% of the theoretical yield by treating the acid (2 mols.), in ice-cold pyridine, with thionyl chloride (1 mol.) and keeping the mixture at the ordinary temperature for 3 hrs. The anhydrides are isolated either by pouring into cold dilute hydrochloric acid, or by fractional distillation of the reaction mixture. Almost quantitative yields are obtained with *p*-toluic acid and anisic acid, but the method fails with palmitic, stearic, phenylacetic, *o*- and *p*-nitrobenzoic, and 3 : 5-dinitrobenzoic acids. R. B.

Internally Complex Borates. A. ROSENHEIM and H. VERMEHREN (*Ber.*, 1924, **57**, [*B*], 1337—1342).—The constitution of a series of borates is most simply explained by regarding them as complex salts of tervalent boron in which the element, as in the anion BF_4', has the co-ordination number 4.

Analysis of the *sodium*, *potassium*, *lithium*, *calcium* ($+6H_2O$), and *copper* salts of Jahn's "borodisalicylic acid" are in agreement with the structure $R[C_6H_4<^{O}_{CO_2}>B<^{O}_{CO_2}>C_6H_4]$. Jahn's formulation does not explain the apparent impossibility of forming salts containing two equivalents of alkali. *o*-Hydroxytoluic acid forms well-crystallised compounds with borates of which the *calcium* salt, $C_{32}H_{24}O_{12}B_2Ca,5H_2O$, is described. Glycollic acid yields salts of the formula $\left[\begin{matrix}CH_2\cdot O\\ CO-O\end{matrix}>B<\begin{matrix}O\cdot CH_2\\ O\cdot CO\end{matrix}\right]R$, of which the *potassium*, *ammonium*, *sodium*, and *calcium* compounds are described. Analyses of the pyrocatechol–boric acid derivatives (sodium, potassium, and ammonium salts) agree with the formula

$$[C_6H_4<^{O}_{O}>B<^{O}_{O}>C_6H_4]R,$$

but not with the structure $R_2H_2B_2O_4(C_6H_4O_2)_3$, assigned by Böeseken (A., 1918, i, 219). Similarly, the tartaric acid borates are considered to be internally complex salts (I) rather than boryl derivatives,

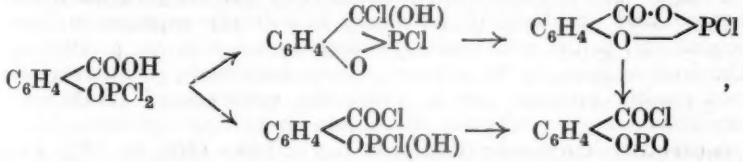
$$CO_2R\cdot CH(OH)\cdot CH(OH)\cdot CO_2\cdot BO;$$

like considerations are extended to the antimonyl compounds. H. W.

$$\left[\begin{matrix}CO\text{-}O\\ CH\cdot O\\ CH\cdot O\\ CO\text{-}O\end{matrix}>B\right]R$$

(I.)

Reaction between the Chlorides of Phosphorus and *o*-, *m*-, and *p*-Hydroxybenzoic Acids. L. ANSCHÜTZ (*Annalen*, 1924, **439**, 265—275).—The constitution of the product of the interaction of phosphorus trichloride and salicylic acid (R. Anschütz and Emery, A., 1887, 947; 1890, 53) is o-*phosphitobenzoyl chloride*, $O{:}PO{\cdot}C_6H_4{\cdot}COCl$. With *p*-toluidine in absolute ether, followed by hydrolysis with hot water, salicyloyl-*p*-toluidide is formed. Traces of phosphine, phosphorous and phosphoric acids were also detected. To test the suggestion that the reaction between phosphorus pentachloride and salicylic acid (cf. R. Anschütz, A., 1906, i, 502) proceeds in two stages, the second being the interaction of phosphorus oxychloride and salicyloyl chloride, the two latter were heated together in equimolar proportions, but no evidence of combination was forthcoming. The alternate suggestion, that with either the trichloride or the pentachloride of phosphorus the phenolic hydroxyl group of the salicylic acid is first attacked, is supported by the ready interaction of phenol and phosphorus trichloride. The following scheme is put forward:



with the corresponding scheme for the interaction between the acid and phosphorus pentachloride.

By heating *m*- or *p*-hydroxybenzoic acid (1 mol.) with phosphorus trichloride (2 mols.) at 120°, no *m*- or *p*-phosphitobenzoyl chloride was obtained. The *o*-phosphitobenzoyl chloride exists in a comparatively stable state, probably owing to a saturation of the partial valency, $C_6H_4<\begin{matrix}CCl{:}O\\O—P{:}O\end{matrix}$. Unsuccessful attempts were made to synthesise phosphitobenzene, PhOPO, from phenoxyphosphorus dichloride and anhydrous oxalic acid at 80—90°, and by the action of benzoic acid on the dichloride at 90°, whereby benzoyl chloride and phenyl benzoate were isolated on subsequent distillation under diminished pressure. A. E. C.

Reduction Product of *o*-Nitromandelonitrile. G. HELLER (*Ber.*, 1924, **57**, [*B*], 1501—1502).—In reply to Reissert and Hessert (this vol., i, 853), the author slightly modifies his original conception (A., 1906, i, 585), but considers the reduction-product of *o*-nitromandelonitrile to be a double hydrochloride of hydroxylaminomandelamide and dihydroxylaminomandelonitrile instead of hydroxylaminomandelamide hydrochloride as proposed by these authors. H. W.

[Benzilic Acid Transformation.] A. SCHÖNBERG (*Ber.*, 1924, **57**, [*B*], 1396—1397; cf. Schönberg and Keller, A., 1923, i, 928).—A reply to the criticisms of Lachman (this vol., i, 653). H. W.

Nitromethylmeconine. W. Rodionow and S. Kagan (*Ber.*, 1924, **57**, [*B*], 1442—1443).—With the object of preparing 5 : 6-dimethoxy-2-ω-nitrovinylbenzoic acid, opianic acid has been condensed with nitromethane. The product, m. p. 166—167°, is, however, stable towards bromine or permanganate, and insoluble in cold but soluble in hot sodium carbonate solution. It is therefore regarded as *ω-nitromethylmeconine*,

$$(OMe)_2C_6H_2\begin{<}\begin{matrix}CH(CH_2\cdot NO_2)\\ CO\end{matrix}\end{>}O.$$

H. W.

Preparation of γ-*o*-Carboxyphenyl-*n*-butyric Acid. W. Hückel and E. Goth (*Ber.*, 1924, **57**, [*B*], 1285—1290).—*Ethyl* 1-*keto*-1 : 2 : 3 : 4-*tetrahydronaphthyl*-2-*glyoxylate*,

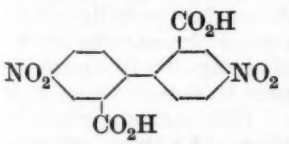
$$\begin{matrix}C_6H_4\cdot CO\\ CH_2\cdot CH_2\end{matrix}\!\!>CH\cdot CO\cdot CO_2Et,$$

m. p. 48°, prepared in 90% yield by the condensation of 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene with ethyl oxalate in the presence of ethyl-alcoholic sodium ethoxide, loses carbon monoxide when heated and yields *ethyl* 1-*hydroxy*-3 : 4-*dihydronaphthalene*-2-*carboxylate*, m. p. 34° (the corresponding *copper* salt, m. p. 196°, and the free *acid*, m. p. 93° [decomp.] are described). The ester does not readily undergo fission under the influence of alkali but is transformed by a solution of sodium in boiling *cyclo*hexanol into γ-*o*-carboxyphenyl-*n*-butyric acid, m. p. 139—140°, in 20% yield; 3 : 4-*dihydronaphthalene*-2-*carboxylic acid*, m. p. 120°, tetrahydro-β-naphthoic acid, m. p. 94°, and 1-naphthol-2-carboxylic acid, m. p. 188°, are simultaneously formed. γ-*o*-Carboxyphenyl-*n*-butyric acid is smoothly hydrogenated in the presence of spongy platinum to γ-*o*-*carboxy*cyclo*hexyl*-n-*butyric acid*, m. p. 92—94°. 1-Naphthol-2-carboxylic acid is hydrogenated to 1-hydroxy-5 : 6 : 7 : 8-tetrahydronaphthalene-2-carboxylic acid, m. p. 164—165° (cf. Schroeter, A., 1922, i, 130), which is reduced further with difficulty to 1-*hydroxydecahydronaphthalene*-2-*carboxylic acid*, m. p. 167—168°. Catalytic hydrogenation of ethyl 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylate gives a mixture of ethyl decahydronaphthalene-2-carboxylate (cf. Borsche and Lange, this vol., i, 32) and ethyl 1-hydroxydecahydronaphthalene-2-carboxylate; hydrolysis of the latter ester yields 1-*hydroxydecahydronaphthalene*-2-*carboxylic acid*, m. p. 198°. H. W.

Phenylsuccinic Acid Series. VIII. Resolution of *r*-Diphenylsuccinanilic and *r*-Diphenylsuccino-*p*-toluidic Acids into their Optical Antipodes. H. Wren and R. E. Burrows (*J. Chem. Soc.*, 1924, **125**, 1934—1937).—*r*-Diphenylsuccinanilic acid has been resolved with quinine, the quinine *l*-diphenylsuccinanilate separating first from alcoholic solutions. l-*Diphenylsuccinanilic acid*, m. p. 193—194° (decomp.), resolidifying and melting again at 224—226°, has $[\alpha]_D^{10\cdot2}$ −338·2° in acetone, $[\alpha]_D^{15}$ −350·3° in ethyl alcohol, and on treatment with alcoholic hydrogen chloride yields l-*diphenylsuccinanil*, m. p. 196—196·5°, $[\alpha]_D^{13\cdot6}$ −117·6° (in chloroform), slight racemisation taking place when the dehydration is

effected with acetyl chloride at 40°. On heating at 195°, *l*-diphenylsuccinanilic acid is converted quantitatively into *r*-diphenylsuccinanil (Wren and Williams, T., 1918, **113**, 838). d-*Diphenylsuccinanilic acid* has $[\alpha]_D^3$ +337·8° in acetone; d-*diphenylsuccinanil*, m. p. 196—196·5°, has $[\alpha]_D^{17}$ +121·0° in chloroform. *r*-Diphenylsuccino-*p*-toluidic acid was similarly resolved, the quinine salt of the *d*-acid separating in the first fractions (along with racemate). l-*Diphenylsuccino*-p-*toluidic acid*, m. p. 209—209·5°, $[\alpha]_D^{18\cdot8}$ −329·5° (in acetone) with alcoholic hydrogen chloride yields l-*diphenylsuccino*-p-*tolil*, m. p. 178°, $[\alpha]_D^{16\cdot4}$ −131·5° (in acetone), $[\alpha]_D^{16\cdot4}$ −136·3° (in chloroform), which shows a similar change of crystalline form to the *r*-tolil (Wren and Williams, *loc. cit.*). d-*Diphenylsuccino*-p-*toluidic acid* has $[\alpha]_D^{16}$ +330·0° in acetone. d-*Diphenylsuccino*-p-*tolil*, $[\alpha]_D^{15}$ +131·3°, is rapidly racemised by traces of alkali. As with the active diphenylsuccinic anhydrides (Wren and Still, T., 1915, **107**, 1457), the specific rotations of the active anils and tolils are much lower than those of the acids from which they are derived. R. B.

Diphenic Acid Series. II. H. W. Underwood, jun., and E. L. Kochmann (*J. Amer. Chem. Soc.*, 1924, **46**, 2069—2078; cf. this vol., i, 176).—The transformation of diphenic acid or its anhydride into fluorenone-4-carboxylic acid previously described is a general reaction for diphenic acid derivatives containing no substituents in the rings. On heating with sulphuric acid, the dichloride, diamide, diethyl ester, dimethyl ester, monoethyl ester, monomethyl ester, monoamide, and imide (obtained by heating the monoamide with glacial acetic acid and acetic anhydride at 130—140°) of diphenic acid are converted into the corresponding fluorenone-4-carboxylic acid derivatives, but hydrolysis occurs in every case, and no conclusions could be drawn regarding the lability of the groups in the side-chains of the diphenic acid derivatives. Isomerisation of phenanthridone does not take place under these conditions, and *pp'*-dinitrophenic acid, which does not form an anhydride, gives no ketone acid, facts which suggest a *trans*-structure for the dinitro-acid (annexed formula), and also that the meta-orientating nitro group loosens the hydroxyl in the carboxyl group (since *m*-nitrobenzoyl chloride is more reactive than benzoyl chloride) and strengthens the bond holding the hydrogen atom in the latter group as well as that holding the ring hydrogen meta to the nitro group.



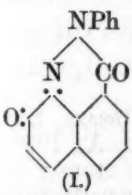
Phenoldiphenein is not isomerised by heat or fuming stannous chloride, but carbon dioxide is evolved at 260—270°. Phenoldiphenein does not give an oxime under the conditions employed for phenolphthalein. In the oxidation of phenanthrene with sodium or potassium dichromate and sulphuric acid, the maximum yield (56%) of phenanthraquinone was obtained with a 350% excess of potassium dichromate. Oxidation of phenanthraquinone gave a maximum yield of diphenic acid (76%) with a 750% excess of potassium dichromate in glacial acetic acid. R. B.

Dipheneins from Resorcinol and Substituted Diphenic Anhydrides. Structure of certain Diphenyl Derivatives. H. ADKINS, E. F. STEINBRING, and (MISS) E. PICKERING (*J. Amer. Chem. Soc.*, 1924, **46**, 1917—1924; cf. A., 1923, i, 578).—Anhydrides of substituted diphenic acids may be prepared when acetamido groups are present in the 4 : 4′- or 6 : 6′-positions, but not when the substituents are nitro or hydroxy groups. The views of various investigators as to the reason for this are discussed. The formation or non-formation of anhydrides is apparently dependent on whether the substituents cause the diphenyl rings to be superimposed or extended (cf. Kaufler, A., 1907, i, 307). The rings are apparently superimposed in the case of diphenic acid and of the amino derivatives of diphenyl but are extended in the case of the nitro or hydroxy derivatives. The 4 : 4′-diaminodiphenic acid, m. p. 250—251°, of Hummel, is shown to be impure. A method is described which furnishes the hydrochloride in fine, white needles, and the free acid as a white solid of m. p. 265°. 4 : 4′-*Diacetamidodiphenic anhydride*, white needles which do not melt, is prepared by refluxing the above hydrochloride with acetic anhydride. Heating with ammonia converts it into 4 : 4′-*diacetamidodiphenamic acid*, $C_{18}H_{17}O_5N_3$. Treatment with sodium hypobromite transforms the last into 2 : 7-*diacetamidophenanthridone*, $NHAc\cdot C_6H_3\cdot\overset{CO\text{—}NH}{\underset{}{C_6H_3}}\cdot NHAc$, which darkens but does not melt at 350°. 4 : 4′-Diaminodiphenic acid forms a *tetrazonium chloride*, which on hydrolysis gives 4 : 4′-dihydroxydiphenic acid, pure white crystals, m. p. 278° (Schmidt and Scholl describe it as yellow, m. p. 271—272°). 6 : 6′-*Diaminodiphenic acid hydrochloride*, prepared by reducing the corresponding dinitro derivative, forms white crystals; the free *acid* has m. p. 312—313° (decomp.). 6 : 6′-*Diacetamidodiphenic anhydride* is much less stable than the 4 : 4′-isomeride and readily forms the acid on exposure to moisture. Condensation of these substituted anhydrides with resorcinol in the presence of zinc chloride at 110° results in dipheneins. When higher temperatures are employed, the 4 : 4′-diacetamidodiphenic anhydride appears to change to the isomeric fluorenone-4-carboxylic acid, which condenses to form a fluorescein derivative having a free carboxyl group. This rearrangement is not possible in the case of the 6 : 6′-derivative. All these condensation products are fluorescent, although not so markedly as fluorescein. The *condensation product* of 4 : 4′-diacetamidodiphenic anhydride and resorcinol at 110° is a light red powder, which dissolves in dilute alkali to a reddish-brown solution with green fluorescence. On acetylation with boiling acetic anhydride, a dark red solid is obtained, insoluble in sodium carbonate solution. Similar acetylation of the condensation product made at 160—180° gives a *substance*, $C_{40}H_{32}O_{12}N_2$, soluble in sodium carbonate. Condensation of the 6 : 6′-derivative with resorcinol at 110° gives a similar fluorescent product which after acetylation is insoluble in sodium carbonate solution. A *tetrabromo* compound, $C_{30}H_{18}O_7N_2Br_4$,

was prepared from a condensation product of the 4 : 4′-anhydride at 135—150°; it forms a red, amorphous powder. The results obtained by Underwood and Kochmann (this vol., i, 176) are criticised. A. C.

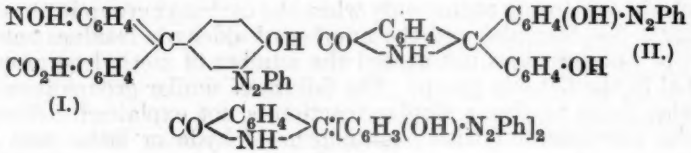
The Three Isomeric Naphthol-1 : 8-dicarboxylic Acids and their Azo Derivatives. Abnormal Coupling Reactions in the Naphthalene Series. K. Dziewoński and T. Stolyhwo (*Ber.*, 1924, **57**, [*B*], 1540—1546).—4- and 2-Naphthol-1 : 8-dicarboxylic acids are distinguished from the 3-hydroxy compound by the marked mobility of the carboxyl group in the ortho or para position to the hydroxyl; this suffers replacement during coupling with diazonium chlorides.

2-*Naphthol*-1 : 8-*dicarboxylic anhydride*, m. p. 350—351°, is prepared by fusing 2-sulphonaphthalene-1 : 8-dicarboxylic acid (cf. Dziewoński and Stolyhwo, this vol., i, 1178) with potassium hydroxide. Its constitution is established by its difference from the other two known naphtholdicarboxylic acids. It couples with benzenediazonium chloride in weakly alkaline solution to form 8-benzeneazo-7-naphthol-1-carboxylic acid, which is isomerised by warm acids into the quinonehydrazone form and thence into


(I.)

1 : 8-*phenylpyridazone*-2-*naphthaquinone* (I), m. p. 201—202°; the latter substance is reconverted into 8-benzeneazo-7-naphtholcarboxylic acid by treatment with alkali hydroxide. 4-Naphthol-1 : 8-dicarboxylic acid and benzenediazonium chloride yield 8-benzeneazo-5-naphthol-1-carboxylic acid, which is transformed by acids into 1 : 8-*phenylpyridazone*-4-*naphthaquinone*, m. p. 238—240°. 3-Naphthol-1 : 8-dicarboxylic acid, on the other hand, couples normally with benzenediazonium chloride, yielding 4-*benzeneazo*-3-*naphthol*-1 : 8-*dicarboxylic anhydride*, m. p. 260—261°. H. W.

Phthaleins. V. Constitution of the Oximic and Iminic Compounds of Phenolphthalein. B. Oddo and D. Curti (*Gazzetta*, 1924, **54**, 572—581).—Coupling with diazonium salts having proved of advantage in determining the structure of the phthaleins (A., 1913, i, 1110; 1916, i, 87), this method is now applied to the oxime and imide of phenolphthalein. Into the former it is found possible to introduce only one azo group, whereas the imide gives both mono- and bis-azo compounds. This difference in behaviour is regarded as due to the structure being respectively quinonoid and lactoid in the two cases, the azo compounds having the following formulæ:


(I.) (II.)

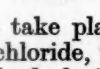
(III.)

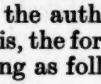
which are in agreement with the formation of a diacetyl compound by the first, and of a triacetyl compound by each of the last two.

When prepared in the ordinary way, phenolphthaleinoxime is always accompanied by *p*-hydroxyphthalanil (cf. Piutti, A., 1886, 1026), which Meyer (A., 1899, i, 707) obtained by the action of excess of hydroxylamine hydrochloride on the oxime in aqueous alcoholic solution and regarded as formed by way of the dioxime, in accordance with the scheme :

$$C_6H_4[C(:NOH)\cdot C_6H_4\cdot OH]_2 \longrightarrow C_6H_4(CO\cdot NH\cdot C_6H_4\cdot OH)_2 \longrightarrow$$
$$C_6H_4\langle \begin{matrix} CO \\ CO \end{matrix} \rangle N\cdot C_6H_4\cdot OH + C_6H_4(NH_2)\cdot OH.$$

Since this reaction does not take place when free hydroxylamine is used in place of its hydrochloride, the author considers that the hydrochloric acid first effects hydrolysis, the formation of *p*-hydroxyphthalanil and *p*-aminophenol resulting as follows :

(1) $CO_2H\cdot C_6H_4\cdot C(C_6H_4\cdot OH):C$  $C:NOH + H_2O \longrightarrow$

$CO_2H\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot OH + H_2N$  $:NOH \longrightarrow C_6H_5\cdot NH\cdot OH,$

which undergoes ready isomerisation into *p*-aminophenol.

(2) $CO_2H\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot OH \longrightarrow CO_2H\cdot C_6H_4\cdot C(:NOH)\cdot C_6H_4\cdot OH \longrightarrow$
$CO_2H\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4\cdot OH \longrightarrow C_6H_4\langle \begin{matrix} CO \\ CO \end{matrix} \rangle N\cdot C_6H_4\cdot OH.$

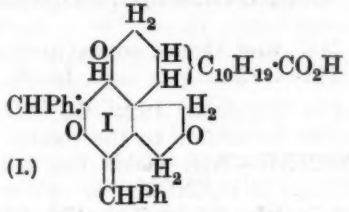
The fact that dichlorophenolphthalein yields, not a bisazo, but only a monoazo compound (cf. Consonno and Apostolo, A., 1921, i, 346), may be due to the presence of the two chlorine atoms; it cannot, therefore, be taken as a proof of the quinonoid constitution of phenolphthalein and its salts.

Benzeneazophenolphthaleinoxime, I, m. p. 202°, forms a *diacetyl* compound, m. p. 231—233°. Treatment of the oxime with excess of benzenediazonium chloride results in the formation of a yellow, crystalline *compound*, m. p. 230—231°. *Benzeneazophenolphthaleinimide*, II, pale yellow crystals, has m. p. 248—250°, and its *triacetyl* derivative, orange-yellow crystals, m. p. 183°. *Bisbenzeneazophenolphthaleinimide*, III, forms small, brownish-yellow crystals, m. p. 270—272°, and its *triacetyl* derivative, a brown, crystalline powder, m. p. 207—208°. T. H. P.

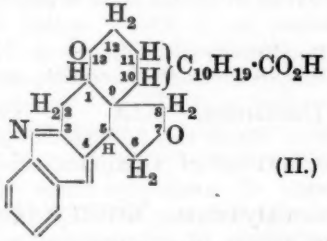
Bile Acids. VI. Condensation of some Ketonic Acids of the Cholic Acid Group with Aromatic Aldehydes and with Isatin. W. Borsche and R. Frank (*Ber.*, 1924, **57**, [*B*], 1373—1380).—Condensation between aldehydes and certain acids of the cholic acid group occurs only when the carbonyl group is present in ring I (see formula) and the number of aldehyde residues entering the molecule does not exceed the number of methylene groups vicinal to the ketonic group. The failure of similar groups present in other rings to give a similar reaction is not explained. Analogously, condensation with *o*-aminobenzaldehyde or isatic acid to derivatives of quinoline occurs only when the group $\cdot CO\cdot CH_2\cdot$

is present in ring I. Further examples are thus afforded of the failure of "typical" reactions when applied to complex compounds.

Dehydrocholic acid is converted by benzaldehyde in the presence of aqueous sodium hydroxide into *dibenzylidenedehydrocholic acid* ($+H_2O$) (I), m. p. above 195°. *Dianisylidenedehydrocholic acid* is also described. With *o*-aminobenzaldehyde dehydrocholic acid yields 7 : 13-*diketo*-3 : 4(2′ : 3′)-*quinocholanic acid* (II), m. p. 296° (the corresponding *hydrochloride*, m. p. 264° after softening at 208°, *methyl* ester, m. p. 215°, and *dioxime*, m. p. 317°, are



(I.)



(II.)

described), whereas with isatin it gives 7 : 13-*diketo*-4-*carboxy*-3 : 4(2′ : 3′)-*quinocholanic acid*, m. p. 297° (decomp.) after previous darkening and softening [*dimethyl* ester; *monoxime*, m. p. 299° (decomp.); *monosemicarbazone*, m. p. 298° (decomp.)]. Dehydrodeoxycholic acid yields *dibenzylidenedehydrodeoxycholic acid*, $C_{38}H_{44}O_4,2H_2O$, m. p. (indefinite) above 95°, *di*-p-*chlorobenzylidenedehydrodeoxycholic acid*, 7-*keto*-3 : 4(2′ : 3′)-*quinocholanic acid*, m. p. 253°, and 7-*keto*-4′-*carboxy*-3 : 4(2′ : 3′)-*quinocholanic acid*, m. p. 298°. 7 : 13-Diketocholanic acid could not be caused to react with benzaldehyde, anisaldehyde, *p*-chlorobenzaldehyde, *o*-aminobenzaldehyde, or isatin, whilst bilianic or deoxybilianic acid did not condense with benzaldehyde, anisaldehyde, *o*-aminobenzaldehyde, or isatin. Pyrodeoxybilianic acid (cf. Wieland and Kulenkampff, A., 1921, i, 112) gives *benzylidenepyrodeoxybilianic acid*, $C_{30}H_{38}O_4$, m. p. 244—245° ($+CH_3\cdot CO_2H$, m. p. 238°), *anisylidinepyrodeoxybilianic acid*, m. p. 270° after softening at 265°, p-*chlorobenzylidenepyrodeoxybilianic acid*, m. p. 282—284° after darkening at 260°, and p-*nitrobenzylidenepyrodeoxybilianic acid*, m. p. 296° (decomp.). *Pyroisodeoxybilianic acid* yields *anisylidenepyroisodeoxybilianic acid*, $C_{31}H_{40}O_5$, m. p. 181°, and p-*nitrobenzylidinepyroisodeoxybilianic acid*, m. p. indefinite, 150—190°. H. W.

Constitution of the Bile Acids. VII. A Ketone, $C_{22}H_{32}O$, from Deoxybilianic Acid. W. Borsche (*Ber.*, 1924, **57**, [*B*], 1435—1436).—Distillation of deoxybilianic acid under 10—15 mm. pressure yields pyrodeoxybilianic acid (cf. Wieland and Kulenkampff, A., 1921, i, 112) and small quantities of a *ketone*, $C_{22}H_{32}O$, m. p. 143°. The latter substance combines with bromine, gives an *oxime*, m. p. 169—170°, and a 2-*nitro*-4-*cyanophenylhydrazone*, m. p. 258—259° (decomp.). The *anisylidene* derivative has m. p. 215—219°. H. W.

Constitution of the Bile Acids. VIII. Acylation of Cholic Acid. W. BORSCHE [with R. FRANCK, O. WEICKERT, and F. HALLWASS] (*Ber.*, 1924, **57**, [*B*], 1620—1622).—Triacetylcholic acid, $C_{30}H_{46}O_8$, m. p. 257° (cf. Wieland and Boersch, A., 1921, i, 178) is prepared in 30—35% yield by the action of acetyl chloride on a solution of cholic acid in glacial acetic acid; the *methyl* ester has m. p. 180—181°. Acylation of cholic acid in the presence of pyridine gives mainly monoacyl derivatives even when an excess of the reagent is used. The following compounds are described: *methyl* 3-*carbethoxycholate*, m. p. 147°, which is oxidised by chromium trioxide in acetic acid solution to *methyl carbethoxyreductodehydrocholate*, m. p. 125°; *methyl* 3-*anisoylcholate*, m. p. 188°; *methyl* 3-p-*nitrobenzoylcholate*, m. p. 217—218°, and thence *methyl* p-*nitrobenzoylreductodehydrocholate*, m. p. 191—192°. H. W.

Dioximes. XIX. L. AVOGADRO (*Gazzetta*, 1924, **54**, 545—550).—Since the addition of ammonia or aniline to the oxides of the nitriles of α-oximino-acids, NOH:CR·CNO, yields the labile forms of aminoglyoximes, NOH:CR·C(NH$_2$):NOH, or phenylaminoglyoximes, NOH:CR·C(NHPh):NOH (A., 1923, i, 472, 855), the action of magnesium methyl iodide on these nitrile oxides should give the analogous forms of the methylglyoximes. The existence of a labile form of phenylmethylglyoxime (cf. A., 1923, i, 1137; this vol., i, 294) may therefore be expected. Such a labile α-phenylmethylglyoxime is formed by reducing phenylmethylglyoxime peroxide by means of zinc dust and acetic acid, but, owing to the readiness with which it undergoes isomerisation into the ordinary or β-form, it is best prepared as nickel compound by treating the reduced peroxide in alcoholic solution with nickel acetate and ammonia solutions, the nickel being eliminated by means of dilute hydrochloric acid in presence of ether.

Stable or β-phenylmethylglyoxime forms a *diacetyl* compound, NOAc:CMe·CPh:NOAc, m. p. 88—89°, and a *dibenzoyl* compound, m. p. 171°. *α-Phenylmethylglyoxime*, m. p. 140—141°, is converted into the β-form by traces of extraneous substances or, more rapidly, by heating either alone above its melting point or with dilute acetic acid. It dissolves without coloration in dilute sodium hydroxide solution, and is reprecipitated unchanged by carbon dioxide. Concentrated sulphuric acid converts it into the anhydride, *phenylmethylfurazan*, O$<$N:CMe / N:CPh, a colourless liquid heavier than water and of characteristic odour. When treated either with nitrogen peroxide or with sodium hypochlorite in sodium hydroxide solution, it undergoes dehydrogenation to phenylmethylglyoxime peroxide. The *nickel* compound, probably $C_9H_8O_2N_2Ni$, forms a yellowish-green precipitate but was not obtained pure. The *diacetyl* derivative has m. p. 100—101° with previous softening, and the *dibenzoyl* derivative, m. p. 120°.

T. H. P.

Dioximes. XX. G. RUGGERI and G. RIGOLI (*Gazzetta*, 1924, **54**, 550—556).—In view of the fact that the two forms of phenyl-

glyoxime behave differently towards nitrogen peroxide, concentrated sulphuric acid, diazonium salts, nickel, copper, and cobalt salts, etc., diversity in their behaviour towards reducing agents also is to be expected (cf. A., 1923, i, 471, 856); since only the β-modification is a true dioxime, this alone should yield phenylethylenediamine on reduction. Feist and Arnstein (A., 1895, i, 274) obtained this diamine by the action of sodium and alcohol on phenylglyoxime, but the latter probably consisted of a mixture of the α- and β-forms, and the product obtained differs from Purgotti's so-called phenylethylenediamine, formed by the action of zinc and hydrochloric acid on ω-cyanobenzylamine (A., 1895, i, 345). The authors find that this amine is not reducible under such conditions, so that the benzoyl compound and chloroplatinate described by Purgotti are not derivatives of phenylethylenediamine. When heated with either sodium and alcohol or hydriodic acid and red phosphorus, ω-cyanobenzylamine yields ammonia, hydrocyanic acid, benzaldehyde, and other products not identified; with sodium amalgam in aqueous alcoholic solution kept neutral by means of acetic acid, traces of phenylethylenediamine are obtainable, but, in the cold, aluminium amalgam in ethereal solution, stannous chloride and hydrochloric acid, or red phosphorus and hydriodic acid are without sensible action.

Either modification of phenylglyoxime yields phenylethylenediamine when treated with sodium in alcoholic solution, but benzoyl cyanide oxime is probably formed as an intermediate product. By hydriodic acid and red phosphorus, both forms of the glyoxime are converted into ω-aminoacetophenone, which is formed also from benzoyl cyanide oxime under the same conditions; the use of this reducing agent with oximino compounds is preferable to that of others as it furnishes directly hydriodides of amino derivatives, these being sparingly soluble and readily separable. Reduction of both α- and β-phenylglyoxime in ethereal solution by means of aluminium amalgam gives diphenylpyrazine, which is a product of the condensation of ω-aminoacetophenone; similar reduction of benzoyl cyanide oxime gives cyanobenzylamine.

ω-*Aminoacetophenone phenylhydrazone*, $NH_2 \cdot CH_2 \cdot CPh{:}N_2HPh$, has m. p. 153° (slight decomp.), and *benzoyl-ω-aminoacetophenone*, $NHBz \cdot CH_2Bz$, m. p. 125°.

Cyanobenzylamine forms a *picrate*, $NH_2 \cdot CHPh \cdot CN, C_6H_3O_7N_3$, m. p. 160—161° (decomp.), and a *benzoyl* derivative, m. p. 159—160°. T. H. P.

***s*- and *as*-Dimethyl[*cyclo*]pentanones.** A. Haller and R. Cornubert (*Compt. rend.*, 1924, **179**, 315—320).—In continuation of previous work (cf. A., 1914, i, 291; also A., 1923, i, 92 for complete list of papers) it is confirmed that the dimethyl*cyclo*pentanone obtained by the alkylation of 1-methyl*cyclo*pentan-5-one is the unsymmetrical ketone by the preparation both of the symmetrical 1 : 4-dimethyl*cyclo*pentan-5-one from *ethyl* 1 : 4-*dimethyl*cyclo*pentan*-5-*one*-4-*carboxylate*, b. p. 121°/32 mm., d_4^{15} 1·0157, n_D^{15} 1·4431 (the preparation of which from ethyl *cyclo*pentanonecarboxylate is

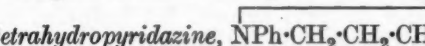
outlined), and of the unsymmetrical 1 : 1-dimethyl*cyclo*pentan-5-one obtained by Blanc (A., 1908, i, 654); and by the preparation of their oximes, semicarbazones, and benzylidene derivatives. The physical constants of the two dimethyl ketones have been redetermined; the 1 : 1- has b. p. 143—144° (corr.)/740 mm., $d_4^{19\cdot5}$ 0·8938, n_D 1·4322; the 1 : 4-, b. p. 147°/744 mm., $d_4^{17\cdot5}$ 0·8918, n_D 1·4312. Condensed with benzaldehyde in the presence of hydrochloric acid the symmetrical ketone yields a *compound* $C_{21}H_{22}O_2$, m. p. 129·5°, obtained by the loss of 1 mol. of water from 2 mols. of benzaldehyde and 1 mol. of ketone; it is the lower homologue of the corresponding *cyclo*hexanone compound, $C_{22}H_{24}O_2$ (cf. A., 1920, i, 390). The unsymmetrical ketone yields benzylidene-1 : 1-dimethyl*cyclo*pentan-5-one, m. p. 36°, together with a brown, viscous residue having a b. p. corresponding with that of the compound, $C_{21}H_{22}O_2$. The oxime of 1 : 4-dimethyl*cyclo*pentan-5-one is an uncrystallisable liquid, b. p. 11·5°/33 mm., and has a camphor-like odour when hot; that of the unsymmetrical ketone has m. p. 65·5° (Blanc, *loc. cit.*, gives 69°). A study of the semicarbazone of the product of alkylation of 1-methyl*cyclo*pentan-5-one shows that this consists mainly of the 1 : 1-dimethyl- together with a small quantity of the 1 : 4-dimethyl-*cyclo*pentan-5-one. J. W. B.

Conversion of Hydroaromatic into Aromatic Compounds. I. Action of Chlorine on 5-Chloro-1 : 1-dimethyl-Δ^4-*cyclo*hexen-3-one. L. E. Hinkel (*J. Chem. Soc.*, 1924, **125**, 1847—1855).—The difference between the action of chlorine and bromine on the same hydroaromatic compound previously recorded (T., 1920, **117**, 1296) has now been observed in the case of 5-chloro-1 : 1-dimethyl-Δ^4-*cyclo*hexen-3-one (cf. Crossley and Renouf, T., 1914, **105**, 169), which on treatment with chlorine in cold chloroform solution yields 4 : 5-*dichloro*-1 : 1-*dimethyl*-Δ^5-cyclo*hexen*-3-*one*, a liquid with a camphoraceous odour, b. p. 120—121°/13 mm. The dichloroketone on heating loses hydrogen chloride and is converted into 5-chloro-*o*-3-xylenol (Hinkel and others, T., 1923, **123**, 2968). Alcoholic potassium hydroxide converts it into the same compound, whilst on heating with sulphuric acid 6-*chloro*-o-4-*xylenol*, m. p. 98° (*benzoate*, m. p. 42°), is obtained. The structure of the last is established by its synthesis from 5-nitro-*o*-3-xylidine, which is converted by the diazo reaction into 6-*chloro*-4-*nitro*-o-*xylene*, m. p. 101°, giving on reduction 6-*chloro*-o-4-*xylidine*, m. p. 72°, from which 6-chloro-*o*-4-xylenol is obtained by diazotisation of the sulphate. On treatment of the dichlorohexenone with chlorine in chloroform solution there is obtained 3 : 4 : 5-*trichloro*-1 : 1-*dimethyl*-Δ^4-cyclo*hexen*-3-*one*, m. p. 61°, the main product of the action of chlorine on 5-chloro-1 : 1-dimethyl-Δ^4-*cyclo*hexen-3-one at the ordinary temperature. On treatment with alcoholic potassium hydroxide, the trichlorohexenone yields 4-*chloro*-3 : 5-*dihydroxy*-o-*xylene*, m. p. 123° (*dibenzoate*, m. p. 137°); sulphuric acid converts it into 5 : 6-*dichloro*-o-4-*xylenol*, m. p. 102° (*benzoate*, m. p. 94°), which with chlorine in light petroleum yields the *trichloro*-o-4-*xylenol*, m. p. 182·5° (*benzoate*, m. p. 120°), obtained by the action

of chlorine on 6-chloro-*o*-4-xylenol; whilst on heating with quinoline at 170°, 4 : 5-*dichloro*-o-3-*xylenol*, m. p. 95° (*benzoate*, m. p. 128°, *tetrachloro* derivative, $C_8H_6OCl_4$, m. p. 127·5°), is obtained.

The liquid from which the trichlorohexenone separates on distillation yielded a fraction, b. p. 145—155°/13 mm., from which 2 : 4 : 5 : 6-*tetrachloro*-1 : 1-*dimethyl*cyclo-Δ^4-*hexen*-3-*one*, m. p. 91°, was obtained, probably formed from the dichloroketone by chlorination and loss of hydrogen chloride, since the trichloroketone is not further attacked by chlorine in boiling chloroform solution. On treatment with alcoholic potassium hydroxide, the tetrachloroketone yields a *dichloroxylenol*, $C_8H_8OCl_2$, m. p. 119—120° (*benzoyl* derivative, m. p. 129°), whilst with sulphuric acid a mixture of trichloro-*o*-3- and -*o*-4-xylenols is obtained. R. B.

Phenyl γ-Chloropropyl Ketone. J. B. CONANT, J. B. SEGUR, and W. R. KIRNER (*J. Amer. Chem. Soc.*, 1924, **46**, 1882—1885).—The ketone was synthesised from trimethylene glycol in the following steps: $OH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH \rightarrow CH_2Cl{\cdot}CH_2{\cdot}CH_2{\cdot}OH \rightarrow CH_2Cl{\cdot}CH_2{\cdot}CH_2Br \rightarrow CH_2Cl{\cdot}CH_2{\cdot}CH_2{\cdot}CN \rightarrow CH_2Cl{\cdot}CH_2{\cdot}CH_2{\cdot}COPh$. The yields for successive steps were 65%, 70%, 42%, and 50%, giving an over-all yield on the glycol of about 9% of the theoretical. *Phenyl γ-chloropropyl ketone*, m. p. 19—20°, prepared by the interaction of ethereal solutions of γ-chlorobutyronitrile and magnesium phenyl bromide at 0°, has no lachrymatory properties, in contrast to the α-chloroketones. The best method of identifying the ketone is through its condensation product with phenylhydrazine,



1 : 3-*diphenyltetrahydropyridazine*, $NPh{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CPh{\cdot}NH$, m. p. 138—139°. Benzoyl*cyclo*propane was obtained in good yield by the action of potassium hydroxide in methyl alcohol on the ketone at the ordinary temperature; the tendency to form this *cyclo*propane may account for the low yield in the last step of the synthesis. A. C.

***CC*-Phenylalkylmethane Dialkylsulphones.** CHEMISCHE FABRIK VON HEYDEN AKT.-GES. (D.R.-P. 376472; from *Chem. Zentr.*, 1924, i, 965).—The sulphones described are obtained by condensing ketones with alkylmercaptans and oxidising the resulting mercaptols. The following compounds are mentioned: *αα-diethylthiol-α-phenylpropane*, $CPhEt(SEt)_2$, a light yellow oil, which on oxidation yields *αα-diethylsulphone-α-phenylpropane*, $CPhEt(SO_2Et)_2$, crystals, m. p. 115—116°; *αα-diethylsulphone-α-phenyl-*Δ^γ*-butylene*, crystals, m. p. 136—138°. G. W. R.

Indene Series. F. ISHIWARA (*J. pr. Chem.*, 1924, [ii], **108**, 194—199).—2-Bromo-1-hydroxyhydrindene is obtained by boiling indene dibromide with magnesium carbonate in aqueous acetone (cf. Krämer, A., 1891, 205). It is oxidised by dichromate and sulphuric acid to 2-bromo-1-hydrindone, which decomposes explosively at 152°. When boiled with sodium acetate in glacial acetic acid, the latter affords 2-*acetoxy*-1-*hydrindone*, b. p. 128°/0·1 mm., 137°/1·0 mm., 165°/17 mm., 172°/19 mm., which reduces cold Fehling's

solution, and is hydrolysed by potassium carbonate in aqueous methyl alcohol to *2-hydroxy-1-hydrindone*, m. p. 40—40·5° (sinters at 38°), b. p. 95°/0·05 mm., 128—133°/1 mm., which also reduces Fehling's solution, and decomposes on keeping; the *phenylurethane* has m. p. 133—134° after sintering at 129°. It yields 1 : 2-diketohydrindene (cf. T., 1912, **101**, 232) on oxidation with chromic acid, and the *osazone* of this diketone, m. p. 222—223° (cf. Gabriel, A., 1897, i, 61), together with the *substance* $C_{15}H_{14}ON_2$, m. p. 123—124°, on treatment with phenylhydrazine. F. G. W.

Formation of Alcohols and Hydrocarbons by the Catalytic Hydrogenation of Aromatic and Aliphatic-Aromatic Carbonyl Compounds. F. Straus and H. Grindel (*Annalen*, 1924, **439**, 276—312).—The products of hydrogenation of several carbonyl compounds in acetone solution by means of palladium and hydrogen at the ordinary temperature and pressure, have been examined. Only those compounds in which the carbonyl group is in the α-position to the benzene ring can be ultimately reduced to the saturated hydrocarbon, the other carbonyl compounds being reduced to the carbinol. The stages of the reduction may be followed graphically in some cases, by the different rates of absorption of hydrogen. This method of preparation of some of the intermediate reduction products is superior to other reduction methods, for example, the preparation of αγ-diphenylpropyl alcohol. In some cases, mixtures are produced, especially where addition of hydrogen may take place at the 1 : 2- or 1 : 4-positions. Styryl methyl ketone and distyryl ketone, for instance, are only partly reduced to the corresponding carbinols:

$$R\cdot CH{:}CH\cdot COR' \begin{cases} \nearrow R\cdot CH_2\cdot CH{:}C(OH)R' \longrightarrow R\cdot CH_2\cdot CH_2\cdot COR' \\ \searrow R\cdot CH{:}CH\cdot CH(OH)R' \longrightarrow R\cdot CH_2\cdot CH_2\cdot CH(OH)R' \end{cases}$$

and the methoxyl derivatives behave similarly.

Phenyl styryl ketone on reduction yields progressively, phenyl β-phenylethyl ketone, αγ-diphenylpropyl alcohol, and αγ-diphenylpropane. *p*-Anisyl *p*-methoxystyryl ketone yields p-*anisyl* β-p-*methoxyphenylethyl ketone*, m. p. 42—43° (*oxime*, m. p. 116—118·5°, *semicarbazone*, m. p. 148—149°), and finally *αγ-di*-p-*methoxyphenylpropane*, m. p. 45—46°. With 2 mols. of hydrogen a mixture of the saturated ketone, carbinol, and hydrocarbon are produced. Acetophenone yields phenylmethylcarbinol and, more slowly, ethylbenzene, whilst the *p*-methoxy derivative yields a mixture of acetylanisole, anisylmethylcarbinol, and ethylanisole. Benzophenone yields benzhydrol and, finally, diphenylmethane, whilst *pp*-dimethoxybenzophenone with 1 mol. of hydrogen yields a mixture of the ketone and dianisylmethane. Styryl methyl ketone yields phenylethyl methyl ketone, and the *p*-methoxy derivative yields a mixture of *p*-methoxyphenylethyl methyl ketone and δ-*p*-methoxyphenylbutan-β-ol. Phenyl propenyl ketone gives progressively, phenylpropylcarbinol, m. p. 14·5°, and *n*-butylbenzene. Distyryl ketone is partly reduced to the corresponding carbinol, and di-*p*-methoxystyryl ketone is more completely reduced to

di-*p*-methoxyphenylethyl ketone; the carbinol could not be isolated. Cinnamylideneacetophenone gave αε-diphenylpentane in good yield.

Cinnamaldehyde on exhaustive hydrogenation yielded a mixture of hydrocinnamaldehyde and propylbenzene; with 1 mol. of hydrogen, it gave a mixture of propylbenzene, hydrocinnamyl alcohol, and unchanged aldehyde. Cinnamyl alcohol gave the saturated alcohol and a small amount of the hydrocarbon. By exhaustive hydrogenation of cinnamaldehyde by Skita's method in alcoholic solution, the saturated alcohol was the chief product, with a little hydrocinnamaldehyde; with 1 mol. of hydrogen, some of the cinnamaldehyde was unchanged.

Benzaldehyde with 2 mols. of hydrogen yields toluene and with 1 mol. a mixture of benzyl alcohol, toluene, and benzaldehyde.

A. E. C.

Use of Aliphatic Acid Anhydrides in the Preparation of Ketones by the Friedel and Crafts Reaction. C. R. NOLLER and R. ADAMS (*J. Amer. Chem. Soc.*, 1924, **46**, 1889—1896).—The poor results obtained by various workers on substituting acetic anhydride for acetyl chloride in the preparation of ketones by the Friedel and Crafts method is due to the fact that only 1 mol. or less of aluminium chloride was employed. Using 2 or more mols. of the latter, the condensations proceed regularly and smoothly and 80—90% of the theoretical yields (calculated on the results of the first distillation of the crude product) are readily obtainable. Some 19 ketones were prepared, and the only variation in conditions found necessary was an occasional change in the temperature or length of time of reaction. In the case of compounds containing alkoxy groups the splitting of the ether linking is less liable to occur than with acetyl chloride, and rarely amounts to more than 5% of the reaction mixture; using anhydrides other than acetic anhydride, it does not occur at all. In the case of *p*-methyl-ω-chloroacetophenone, the yield is comparatively low; it is better in this case to use chloroacetyl chloride than the chloroanhydride. Incidentally, the methoxyacetonaphthene prepared by Fries (A., 1921, i, 423) is shown to be 2-methoxy-α-naphthyl methyl ketone and the following compounds are described: 4-*Methoxy*-3-*methylacetophenone*, m. p. 26—26·5°, b. p. 116°/3 mm., 273·5°/744 mm.; 2-*methoxy*-5-*methylbutyrophenone*, b. p. 123°/3 mm., 276·5°/739 mm., d_4^{20} 1·0258, n_D^{20} 1·5250; 4-*methoxy*-3-*methylvalerophenone*, m. p. 31—33°, b. p. 151·5°/4 mm., 308·7°/744 mm.

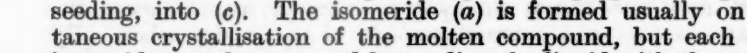
A. C.

Multiple Forms (Pseudopolymorphism) of Derivatives of Phenylethylene, R′R″C:CR‴′Ph. A. GILLET (*Bull. Soc. chim. Belg.*, 1924, **33**, 377—388; cf. this vol., i, 651).—Phenyl β-ethoxystyryl ketone, COPhCH:CPh·OEt, when treated with 1 mol. of bromine in carbon disulphide solution at 0°, and then with a solution of anhydrous potassium acetate in absolute alcohol, gives *phenyl* α-*bromo*-ββ-*diethoxy*-β-*phenylethyl ketone*,

$$COPh{\cdot}CHBr{\cdot}CPh(OEt)_2,$$

m. p. 72°, in 90% yield. The latter compound, when heated at

190—200°/3 mm., gives *phenyl α-bromo-β-ethoxystyryl ketone*, COPh·CBr:CPh·OEt in 70% yield. This compound can be obtained in three isomeric and crystallographically distinct forms, all pale yellow crystals, m. p. (*a*) 64—65°, (*b*) 73°, (*c*) 75·5—76·5°, solubility in methyl alcohol at 18°, (*a*) 17·1, (*b*) 8·5, and (*c*) 6·4%. (*a*) and (*b*) are unstable and change, slowly on keeping and rapidly on seeding, into (*c*). The isomeride (*a*) is formed usually on spontaneous crystallisation of the molten compound, but each of the isomerides can be prepared by seeding the liquid with the required form. The author considers that the existence of two of these isomerides is due to "quinonoid transposition," probably represented by



One of the forms is almost certainly one of two *cis-trans* isomerides and the second geometrical isomeride is being sought. *Phenyl α-bromo-β-methoxystyryl ketone*, prepared similarly to the ethoxy compound, has been obtained in two crystallographically distinct forms, both pale yellow, m. p. (*a*) 63·5—64·5°, (*b*) 71—72°, solubility at 19° in petroleum of b. p. 80—85°, (*a*) 2·84, (*b*) 2·24%, in ethyl alcohol, (*a*) 9·9 at 19°, (*b*) 6·1% at 17°; (*a*) is obtained by spontaneous crystallisation, but is easily converted by seeding into the more stable (*b*); (*a*) can also be obtained by seeding the molten compound with the corresponding isomeride of phenyl dibromo- and di-iodo-styryl ketone. A third (*cis-trans*) isomeride, m. p. 101° (approx.), has been isolated. The isomerides (*a*) and (*b*) of the methoxy compound correspond with (*b*) and (*c*) of the ethoxy compound, respectively. *Phenyl α-bromo-β-propoxystyryl ketone* has been obtained in only one form, m. p. 49°, corresponding with the isomeride (*a*) of the ethoxy compound. Many examples of similar polymorphism already recorded are collected in the paper.

F. G. M.

Correction of the Constitutional Formula of Benzylbenzoin. A. García Banus and J. Pascual Vila (*Anal. Fís. Quím.*, 1924, **22**, 262—263; cf. A., 1922, i, 734).—The product of the reaction of equimolecular portions of magnesium benzyl chloride and benzil, to which the formula $CH_2Ph·CPhBz·OH$ was originally assigned, is now shown to be identical with the benzyl ether of benzoin.

G. W. R.

Action of Nitroxyl on α-Ketoaldehydes. IX. Preparation of α-Ketoformhydroxamic Acids. C. Gastaldi (*Gazzetta*, 1924, **54**, 589—592; cf. A., 1923, i, 1236; this vol., i, 733).—The addition of nitroxyl to the α-ketoaldehydes, phenylglyoxal, $Ph·CO·CH(OH)_2$, and *p*-tolylglyoxal, $C_6H_4Me·CO·CH(OH)_2$, follows the normal course (cf. Angeli, A., 1902, i, 78, 765; 1904, i, 172; 1905, ii, 385). As a reagent for furnishing nitroxyl, benzenesulphonhydroxamic acid yields better results than nitrohydroxylaminic acid. Thus, addition of sodium hydroxide solution to a methyl-alcoholic solution of phenylglyoxal and benzenesulphon-

hydroxamic acid, cooled in ice, yields almost pure sodium benzoylformhydroxamate.

p-*Methylbenzoylformhydroxamic acid*, $C_6H_4Me{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}OH$ or $C_6H_4Me{\cdot}CO{\cdot}C(OH){:}NOH$, prepared from *p*-tolylglyoxal and benzenesulphonhydroxamic acid, has m. p. 112° (decomp.); its *sodium* salt deflagrates when heated. Its α-*oxime*, $C_6H_4Me{\cdot}C(:NOH){\cdot}CO{\cdot}NH{\cdot}OH$ or $C_6H_4Me{\cdot}C(:NOH){\cdot}C(OH){:}N{\cdot}OH$, pale red needles, m. p. 186° (decomp.), gives a deep red coloration with ferric chloride; the yellow *nickel* compound is soluble, and the olive-green *copper* compound insoluble, in dilute acetic acid. The β-*oxime*, obtained by heating the α-modification with dilute acetic acid in presence of nickel acetate and decomposing the nickel compound formed by means of dilute sulphuric acid, m. p. 183° (decomp.), gives a violet-red coloration with aqueous ferric chloride; the *nickel* compound is a voluminous, brick-red precipitate, and the *copper* compound an olive-green precipitate.

T. H. P.

Preparation of Higher Ketones. B. Helferich and L. Keiner.—(See i, 1166.)

Diphenoquinones. K. von Auwers and G. Wittig (*Ber.*, 1924, **57**, [*B*], 1270—1275).—Monohydric phenols containing substituents in the two ortho positions to the hydroxy group resemble *vic.-m*-xylenol (Auwers and Markovitz, A., 1905, i, 219; 1908, i, 629) in being oxidisable to diphenoquinones if the substituents are alkyl groups, but not if phenyl or chlorine is present. The oxidation is best effected by short, vigorous treatment of the phenols with chromium trioxide in boiling glacial acetic acid solution.

3-*Ethyl*-o-*cresol*, b. p. 91—92°/12 mm. (*phenylurethane*, m. p. 147—148°), prepared by the reduction of 3-acetyl-*o*-cresol with amalgamated zinc and hydrochloric acid, is oxidised to 3 : 3′(3 : 5′)-*dimethyl*-5 : 5′(5 : 3′)-*diethyldiphenoquinone*,

$$O{:}C\begin{<}CMe{:}CH\\CEt{:}CH\end{>}C{:}C\begin{<}CH{:}CEt\\CH{:}CMe\end{>}C{:}O,$$

m. p. 153°, which is reduced by zinc dust and dilute acetic acid to 4 : 4′-*dihydroxy*-3 : 3′-*dimethyl*-5 : 5′-*diethyldiphenyl*, m. p. 148° (*dibenzoate*, m. p. 171—172°). 3-Ethyl-*o*-cresol and nitrous acid yield 5-*nitroso*-3-*ethyl*-o-*cresol*, m. p. 135—136°, which is oxidised by potassium ferricyanide to 5-*nitro*-3-*ethyl*-o-*cresol*, m. p. 133—134°.

3-*Propenyl*-o-*cresol*, b. p. 113—115°/12 mm., m. p. 41—42°, obtained by the action of concentrated aqueous potassium hydroxide on 3-allyl-*o*-cresol at 150°, is reduced by sodium and boiling alcohol to 3-*propyl*-o-*cresol*, b. p. 105—107°/12 mm. (*phenylurethane*, m. p. 110—111°). The substance is also prepared by the reduction of 3-*propionyl*-o-*cresol*, b. p. 127—129°/15 mm., m. p. 22—23° (*semicarbazone*, m. p. 202°) by Clemmensen's method, the ketone being obtained together with 5-*propionyl*-o-*cresol*, m. p. 83·5—84°, by the action of aluminium chloride at 120° on o-*tolyl propionate*, b. p. 99°/12 mm. The cresol is transformed by

nitrous acid into *5-nitroso-3-propyl-o-cresol*, m. p. 93—94°, and is oxidised by chromic acid to 3 : 3′(3 : 5′)-*dimethyl*-5 : 5′(5 : 3′)-*dipropyldiphenoquinone*, bluish-green crystals, m. p. 136—137°; the latter is reduced to 4 : 4′-*dihydroxy*-3 : 3′-*dimethyl*-5 : 5′-*dipropyldiphenyl*, m. p. 123·5—125° (*diacetate*, m. p. 95—96°).

4-*Chloro*-2-*ethylphenol*, b. p. 118—119°/12 mm., is converted into the corresponding *acetate*, b. p. 132°/12 mm., which is isomerised by aluminium chloride at 120° to 4-*chloro*-6-*acetyl*-2-*ethylphenol*, b. p. 145—146°/12 mm. (the *sodium* salt and the *semicarbazone*, m. p. 229—230°, are described). The ketone is reduced by zinc and hydrochloric acid to 1-*chloro*-2 : 6-*diethylphenol*, b. p. 128—132°/12 mm., m. p. 31—31·5°, which is converted by sodium and boiling alcohol into 2 : 6-*diethylphenol*, m. p. 37·5—38°. 3 : 5 : 3′ : 5′-*Tetraethyldiphenoquinone* forms bluish-red needles, m. p. 142—143°. H. W.

Naphthaquinone Derivatives. Société Anonyme des Matières Colorantes et Produits Chimiques de Saint-Denis, A. Wahl and R. Lantz (Brit. Pat. 206142).—A 4-arylamino-1-arylimino-β-naphthaquinone is obtained, together with an equivalent of a 1-arylamino-β-naphthol, by the action of a primary aromatic amine on a 1-arylimino-β-naphthaquinone. By the further action of the same, or another, amine, the 1-arylimino group of the naphthaquinone produced may be replaced, when the aryl radical of the amine is different from that of the 1-arylimino group, by an arylimino group derived from the amine, the 4-arylamino group remaining unattacked. In this way, compounds containing the same or different aryl radicals attached to the 1-imino and 4-amino nitrogen atoms can be prepared. By carrying out the reaction in presence of air and a catalyst such as lime, baryta, or cupric oxide, the 1-arylimino-β-naphthol is reoxidised to the 1-arylimino-β-naphthaquinone, so that the latter under these conditions is completely converted into the 4-arylamino-1-arylimino derivative. The same result is obtained by treating a 1-arylamino-β-naphthol with an amine in presence of air and one of the above catalysts. Under these conditions, the products are isolated as pure crystalline derivatives of the metal present. The 4-arylamino-1-arylimino-β-naphthaquinones are hydrolysed by dilute acids to 4-arylimino-2-hydroxy-α-naphthaquinones and are isomerised when boiled in glacial acetic acid to 2-arylamino-4-arylimino-α-naphthaquinones. 4-*Phenylamino*-1-*phenylimino*-β-*naphthaquinone*, brown-red crystals, 4-p-*toluidino*-1-p-*tolylimino*-β-*naphthaquinone*, brown prisms, 4-*phenylamino*-1-p-*tolylimino*-β-*naphthaquinone*, 4-o-*methoxyphenylamino*-1-o-*methoxyphenylimino*-β-*naphthaquinone*, and the copper compounds of the first and last of these are described. F. G. W.

Isomerism of Menthol and *neo*Menthol. G. Vavon and A. Couderc (*Compt. rend.*, 1924, **179**, 405—408).—*d-neo*Menthol is readily prepared by the reduction of *l*-menthone with hydrogen in the presence of platinum black, using acetic acid, ether, or

alcohol as solvent. The velocity of reduction decreases with the solvents in the order named. The separation of the isomerides in the product, ($[\alpha]_{578}$ +4° to +10°) is effected by esterification with succinic anhydride and crystallisation of the *neo*menthyl succinate from aqueous alcohol and aqueous acetic acid to constant rotatory power. d-neo*Menthyl succinate*, m. p. 68°, has $[\alpha]_{578}$ +34·70° (in chloroform), and on hydrolysis yields a *d-neo*menthol, b. p. 107—108°/20 mm., d_4^{22} 0·897, n_D^{22} 1·4594, $[\alpha]_{578}$ +21·95° (cf. Pickard and Littlebury, T., 1912, **101**, 109). The velocity of esterification of *neo*menthol with acetic and butyric acids is much less than that of menthol, the difference being more pronounced at lower temperatures and in the presence of a catalyst (hydrochloric acid). Similarly, the hydrolysis of *neo*menthyl hydrogen succinate by alcoholic potassium hydroxide proceeds much more slowly than that of the corresponding menthol ester. These differences, and the preponderating formation of *neo*menthol in the reduction of menthone, are readily explained by the theory of steric hindrance, when *neo*menthol is regarded as the *cis*- and menthol as the *trans*-form of 1-methyl-4-*iso*propylhexan-3-ol.

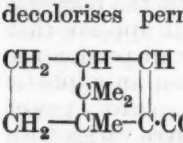
R. B.

Dependence of Optical Rotatory Power on Chemical Constitution. V. Rotatory Dispersions of *d*-Camphorimide, *d*-Camphorbenzylimide, Benzyl-*d*-camphoramic Acid, and their Derivatives. B. K. Singh and A. C. Biswas (*J. Chem. Soc.*, 1924, **125**, 1895—1898).—The rotatory powers of a number of benzyl and substituted benzyl derivatives of *d*-camphorimide and of *d*-camphoramic acid for the wave-lengths 5893, 5780, 5461, have been studied in benzene, ether, chloroform, acetone, ethyl alcohol, and methyl alcohol solution. Substitution of the benzyl group for the imido-hydrogen atom increases the rotatory power. In all cases except camphor-*o*-nitrobenzylimide, the rotatory power is lowest in benzene, which has the lowest dielectric constant, but no regular relation was disclosed between the rotatory powers and the dielectric constants of the other solvents. The rotatory dispersion of *d*-camphorimide and its benzyl derivative is highest in benzene where the rotatory power is lowest, whilst the converse is the case with camphor-*o*-nitrobenzylimide, and it appears that in this series the rotatory power and the rotatory dispersion are influenced in opposite directions by the change from an aliphatic solvent to benzene. The relative magnitude of the rotatory power of camphorbenzylimide and its three nitro derivatives varies with the nature of the solvent. Frankland's rule holds only in chloroform and in benzene, whilst Cohen's rule is valid except in chloroform and in methyl alcohol, the deviation in the latter solvent being very marked. The rotation is increased considerably when the ring structure is opened by hydrolysis, and the following values for $[M]_D$ in ethyl alcohol are given: camphorimide, 10·99°; camphoramic acid, 89·45° (α); 119·4° (β); camphorbenzylimide, 30·19°; benzylcamphoramic acid, 99·88°; camphor-*m*-nitrobenzylimide, 31·92°; 3-nitrobenzylcamphoramic acid, 106·70°.

d-*Camphor*-o-*nitrobenzylimide*, m. p. 131°, from benzyl chloride and camphorimide in alcoholic potassium hydroxide solution, on hydrolysis with potassium hydroxide yields a dark greenish-brown and a brown o-*nitrobenzyl*-d-*camphoramic acid*. d-*Camphor*-m-*nitrobenzylimide*, m. p. 69°, similarly prepared, on hydrolysis yields two colourless m-*nitrobenzylcamphoramic acids*, m. p. 134° and 179°. *d*-Camphor-*p*-nitrobenzylimide similarly yields a brown-orange form, decomp. 250°, and a deep purple-brown form, m. p. above 325°, of p-*nitrobenzoyl*-d-*camphoramic acid*. d-*Benzylcamphoramic acid* has m. p. 149°. R. B.

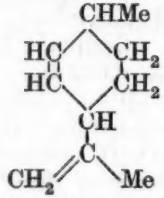
Valency. IV. Absorption Spectra of Camphor, Benzylidenecamphor, and Camphorquinone. Optical Evidence of Two Types of Conjugation. T. M. LOWRY and H. S. FRENCH (*J. Chem. Soc.*, 1924, **125**, 1921—1927).—Quantitative observations of the absorption spectra of camphor and of camphorquinone in alcohol, benzene, and *cyclo*hexane show that the position of the band is almost independent of the solvent and concentration. On passing from camphor to camphorquinone the band at 2880 Å. (alcoholic solution) is shifted to 4650 Å., whilst the molecular extinction coefficient remains practically constant at $\log \epsilon = 1{\cdot}5$. The development of colour is thus not accompanied by any increase in absorptive power. In benzylidenecamphor, the molecular extinction coefficient becomes $\log \epsilon = 4{\cdot}32$, but the wave-length remains at 2900 Å., being practically unaltered by the extension of the conjugated system. It is concluded that benzylidenecamphor and camphorquinone represent two different types of conjugation, and that some additional factor beyond a long conjugated chain is required to produce visible colour. In the quinones, this may be supplied by the presence of two doubly-linked oxygen atoms at the end of a conjugated chain. R. B.

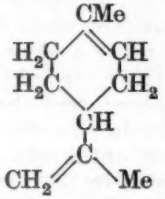
Carbylamines. IX. Reaction of Phenylcarbylamine with Pernitrosocamphor. M. PASSERINI (*Gazzetta*, 1924, **54**, 540—544).—Phenylcarbylamine and pernitrosocamphor interact slowly in the cold, giving nitrous oxide and *d*-bornylene-6-carboxylic anilide. The acid, formed when the anilide is hydrolysed, rapidly decolorises permanganate, readily unites with bromine, and is reduced to *d*-camphane-6-carboxylic acid by hydrogen in presence of platinum black. d-*Bornylene*-6-*carboxylic acid* (annexed formula), has m. p. 65—66°, $[\alpha]_D^{23{\cdot}5}$ (in ethyl acetate) +66·2°; *anilide*, m. p. 124—125°. d-*Camphane*-6-*carboxylic acid* has m. p. 72—74°, $[\alpha]_D^{23{\cdot}5}$ +11·2°, and yields a sparingly soluble *silver* salt. T. H. P.



Diprene, a new Terpene. O. ASCHAN (*Annalen*, 1924, **439**, 221—232).—Isoprene (250 g.) was left in an atmosphere of carbon dioxide in a sealed vessel in the dark for 10 years, and then the residual isoprene (76%) was removed. The viscous, rubber-like residue possessed an odour resembling that of rancid olive oil and contained an oil (7·6 g.) volatile in steam. The non-volatile residue

on distillation under diminished pressure yielded an oil, b. p. below 80°/7 mm. (7 g.). These two fractions were combined and distilled over sodium under normal pressures, whereby after two distillations, three main fractions were obtained: (1) b. p. 171—172°, d_4^{20} 0·8535 (4·2 g.); (2) b. p. 173—173·5°, d_4^{20} 0·8552 (1·6 g.); (3) b. p. 175·5—178°, d_4^{20} 0·8603 (1·2 g.). The first fraction is a new hydrocarbon, $C_{10}H_{16}$, which the author names *diprene*. It gives no reaction for sylvestrene, and no nitrosite, as does dipentene. It yields a *dihydrochloride*, m. p. 51·5—52°, which has an odour of juniper oil, and is not identical with that obtained from dipentene

(I.) 

 (II.)

(m. p. 49—50°) or terpinene (m. p. 51—52°). β-Terpinene, which closely resembles diprene in physical properties, yields a crystalline tetrabromide (Wallach, A., 1908, i, 813), but by the action of bromine on an alcoholic solution of diprene at −10°, an oily tetrabromide is formed, stable towards permanganate, which will not crystallise, and may be a mixture of several stereoisomerides.

It is suggested that in the polymerisation of isoprene to form a dimeric compound, a dipentene would be more likely to be formed than a terpinene, at low temperatures, as the former would involve a smaller structural alteration than the latter. The new terpene probably possesses formula I, which isomerises to dipentene (II) on heating or further distillation. The higher boiling fraction (3) probably contains some dipentene, produced by isomerisation, which would account for the fact that the hydrochloride obtained from this fraction is difficult to crystallise. A. E. C.

Heat of Combustion of Natural and "Sulphuric Acid" Caoutchouc. F. KIRCHHOF and O. MATULKE (*Ber.*, 1924, **57**, [*B*], 1266—1270).—The heat of combustion of plantation pale crêpe rubber is approximately 10,700 cal. per gram. Its empirical formula is $(C_5H_8)_n$, and is therefore identical with that of Congo and synthetic isoprene caoutchouc. The heat of combustion of "sulphuric acid caoutchouc" (cf. Kirchhof, A., 1921, i, 116; 1922, i, 562) is markedly lower than that of natural rubber and depends on the degree of internal polymerisation. The empirical formula of "sulphuric acid caoutchouc," calculated to ash- and sulphate-free material, corresponds very closely with the expression, $(C_{100}H_{160})_nSO_2$. The action of sulphuric acid on resin-free, natural caoutchouc in different media is accompanied by evolution of heat which is approximately proportional in amount to the content of undissolved caoutchouc; the latter is partly depolymerised and oxidised. The transformation (internal polymerisation) is, however, attended by absorption of heat. H. W.

Caoutchouc. II. Hydrocaoutchouc and a Crystalline Form of Caoutchouc. R. PUMMERER and A. KOCH (*Annalen*, 1924, **438**, 294—313).—The following procedure affords samples of caoutchouc of progressively increasing purity, all operations being carried out in an inert atmosphere: (*a*) fractional precipitation from benzene by means of alcohol, the impurities containing oxygen being precipitated in the first fraction, and the solvent removed by extraction with acetone; (*b*) as in (*a*) followed by fractional precipitation from hexahydrotoluene by means of acetone; (*c*) treatment of the product from (*b*) in light petroleum solution with methyl-alcoholic potassium hydroxide, the ethereal solution of the product then being shaken with charcoal. The product from (*a*) gives a clear solution in benzene, turbid in hexahydrotoluene, ether, or light petroleum; that from (*b*) is clear in hexahydrotoluene; and that from (*c*) is clear in all four solvents, and sufficiently pure for direct cold catalytic hydrogenation. On cooling the product obtained as in (*a*) after extraction with acetone, crystals were formed in the rubber mass, the occurrence of three types of crystals in six modifications being ascribed to the presence of several chemical individuals in the purified product. The benzene–alcohol mother-liquors deposited, on keeping, further fractions of caoutchouc which gradually set to a mass of yellowish-white, spherical aggregates, non-crystalline material being removable by washing in ether, from which solvent recrystallisation could also be effected. The crystals became transparent and plastic at 60°, complete fusion taking place at 92°. The sample became partly isotropic at 44°, completely isotropic at 60—62°. The crystalline material is practically non-elastic. Molecular-weight determinations gave negative results.

Caoutchouc purified by method (*c*), above, absorbs hydrogen in cold hexahydrotoluene solution, in presence of spongy platinum, the reaction product, after removal of the platinum, being slightly opalescent and completely stable to air, bromine, or permanganate at the ordinary temperature. On evaporation of the ethereal solution, the hydrocaoutchouc is obtained as an opaque, viscous, non-elastic, partly crystalline mass, $(C_5H_{10})_x$, which does not depress the melting point of camphor. When heated for 3 hours at 200°, then for 20 mins. at 300°, in carbon dioxide at 12 mm. pressure, no visible change takes place, but the product shows a molecular weight of 1700. The crude hydrocaoutchouc was partly distilled at 350° (bath temperature) in hydrogen at 1 mm., slight decomposition taking place only at first. The distillate, comprising one-third of the whole, had a slight odour of limonene, and was unsaturated. It was purified by solution in acetone, followed by treatment with charcoal in ether, to a colourless, saturated hydrocarbon, $C_{45}H_{92}$. The composition of the undistilled residue, which was colourless and completely saturated, corresponded with the formula $(C_5H_{10})_x$, the molecular weight (in camphor) being 1500. It had b. p. 354°/1·5 mm., the purified distillate forming a viscous, colourless mass, $C_{50}H_{102}$.

When treated with hydrogen containing 5% of oxygen, in

presence of spongy platinum, purified caoutchouc afforded the unsaturated hydrocarbon, $C_{50}H_{86}$, which, however, did not react with bromine.

The bearing of the above results on the constitution is discussed, and a note on the *X*-ray examination of crystalline caoutchouc appended. F. G. W.

Ether-soluble Constituents of Lac-resin. D. N. Gupta (*J. Indian Inst. Sci.*, 1924, **7**, 142—144).—Stick-lac produced by *Lakshadia mysorensis* grown on *Shorea talura*, Roxb., was finely ground and after removal of wax with light petroleum was percolated with ether. The ethereal extract yielded myricyl alcohol, a colouring matter apparently identical with Tschirch's erythrolaccin, and giving analytical values agreeing well with tetrahydroxyanthraquinone, palmitic acid, probably myristic acid, and an unsaturated hydroxy-acid, probably $C_{15}H_{28}(OH)\cdot CO_2H$. Neither mono- nor tri-hydroxypalmitic acid was isolated. P. M.

Amygdalin. III. Synthesis of Natural *l*-Amygdalin. G. Zemplén and A. Kunz (*Ber.*, 1924, **57**, [*B*], 1357—1359).—The substance described previously (this vol., i, 975) as "stable hepta-acetyl-*l*-amygdalic acid" does not react with thionyl chloride or phosphorus pentachloride, whereas it is converted by dry methyl-alcoholic ammonia into *l*-amygdalamide which is isolated as *hepta-acetyl-l-amygdalamide*, m. p. 180—181°, $[\alpha]_D^{24}$ −66·3° in chloroform. It is hence shown to be the lactone of hexa-acetyl-*l*-amygdalic acid. The hepta-acetyl amide is converted by phosphoryl chloride into hepta-acetyl-*l*-amygdalin, $[\alpha]_D^{24}$ −38·1° in chloroform, which is identical with the product from natural amygdalin. The synthesis of the latter substance is rendered complete by the observation that hexa-acetyl-*l*-amygdalolactone is formed by the interaction of bromoacetogentiobiose and silver *l*-mandelate; the main product of the reaction, however, is *hepta-acetylgentiobiosidyl l-mandelate*, $C_6H_5\cdot CH(OH)\cdot CO\cdot C_{12}H_{14}O_{12}Ac_7$, m. p. 177°, $[\alpha]_D^{24}$ −51·76° in chloroform. (Cf. Campbell and Haworth, *J. Chem. Soc.*, 1924, **125**, 1337.) H. W.

***Digitalinum verum*. II.** A. Windaus, A. Bohne, and A. Schwieger (*Ber.*, 1924, **57**, [*B*], 1386—1388; cf. Windaus and Bandte, A., 1923, i, 1107; Kiliani, A., 1916, i, 493).—Analyses of digitalin, m. p. 229°, which is extracted from *Digitalinum verum* by a somewhat modified procedure, are in agreement with the formula $C_{37}H_{58}O_{14}$. The conception of the substance as a simply unsaturated trihydroxylactone in which one hydroxy group is free whilst the remaining two groups are united to dextrose and digitalose residues is confirmed by the observation that it absorbs only 1 mol. of hydrogen with formation of dihydrodigitalin. The hydrolysis of digitalin by dilute acids is accompanied by the loss of 2 mols. of water. H. W.

Saponins of *Polygala amara*. E. Glaser and H. Krauter (*Ber.*, 1924, **57**, [*B*], 1604 1610).—Two saponins are present in *Polygala amara* which can be separated from one another since one is acidic and precipitable with normal lead acetate whereas

the other is neutral and is precipitated with basic lead acetate. Both are dialysable, and neither is hydrolysed by emulsin nor precipitated by ammonium sulphate. The hygroscopic, neutral saponin, $C_{34}H_{52}O_{20}$, has $[\alpha]_D$ +30° in aqueous solution. It is hydrolysed by hydrochloric acid (2%) to 3 mols. of dextrose and the *sapogenin*, $C_{14}H_{22}O_2$, m. p. 201—202°, which is optically inactive; the latter substance contains one carboxyl group, since it readily yields a *methyl* ester, $C_{15}H_{24}O_2$, m. p. 206°, which combines with bromine in chloroform solution to give the *compound* $C_{15}H_{24}O_2Br_4$, thus establishing the presence of two double bonds. Since an acid, $C_{13}H_{21}\cdot CO_2H$, with a normal carbon chain must contain three double bonds in its molecule, the presence of a ring must also be assumed. The acid saponin, $C_{22}H_{36}O_{10}$, is a brown, amorphous powder which is hydrolysed by dilute acid to equimolecular quantities of dextrose and an amorphous, acidic *sapogenin*, $C_8H_{14}O_3$, m. p. 198°, which does not react with bromine.

The reactions, solubilities, and empirical formulæ of the acid and neutral saponins render it probable that they are respectively identical with polygalasic acid and senegin derived from *Polygala senega*. H. W.

Saponin of the Primula Root. L. Kofler and H. Frauendorfer (*Arch. Pharm.*, 1924, **262**, 318—328; compare Masson, A., 1912, ii, 979).—The author has attempted to determine the nature and amount of the saponin present in radix primulæ, using the hæmolytic index of the drug as a measure of its saponin content. The drug used for the investigation was derived from *Primula veris*, and had the hæmolytic index 1 : 16,000. The saponin, prepared from the drug by extraction with 70% alcohol, precipitation with water, and purification by animal charcoal and finally by electrodialysis (compare Kofler and Dafert, this vol., ii, 74), forms a white, microcrystalline powder, m. p. 218—220°, to which is given the name primulinic acid (cf. Masson, *loc. cit.*). It is insoluble in cold water, slightly soluble in hot, and readily soluble in alkaline media, from which it is precipitated by acids. It contains C 55·04%, H 8·03%, and no nitrogen. It has a bitter taste, and induces vomiting. The hæmolytic index of the pure saponin dissolved in physiological saline, with the aid of sodium hydroxide, to neutral solution, is 1 : 190,000. Its physiological reactions are typical of a saponin. The saponin content of the drug is 8·4%, the average content of the commercial drugs being slightly greater than 5%. The solution of the above crystalline saponin in alcohol, on precipitation with ether, yields the substance in the form of a jelly, which while fresh is more soluble in water than the original form, losing this property on standing. It is therefore suggested that there are two forms of primulinic acid, a crystalline form insoluble in water, and an amorphous, soluble form, and this assumption is used to explain various solubility properties of the substance. From an alcoholic extract of the original radix primulæ, after precipitation of the saponin with ether, another substance crystallised out, which the author regards as

the heptahydric alcohol volemitol, and is probably the substance which Hünefeld (*J. pr. Chem.*, 1836 and 1839) called primulin; some authors have regarded this as the saponin of the drug, although it is different from the latter in many ways. The tannin content of radix primulæ is very low. B. F.

Reduction of Sitosterol. Preparation of Dihydrositosterol or Sitostanol. R. J. ANDERSON and F. P. NABENHAUER (*J. Amer. Chem. Soc.*, 1924, **46**, 1953—1956).—Sitosterol having $[\alpha]$ −30·90°, prepared from wheat bran, was reduced by hydrogen in ethereal solution in the presence of platinum black. The reduction product, $C_{27}H_{47}\cdot OH$, colourless, hexagonal plates, m. p. 141—142°, $[\alpha]_D^{20}$ +24·16° in chloroform, was dihydrositosterol. It did not absorb bromine, and gave negative Liebermann–Burchard and Whitby reactions. It is very similar to, if not identical with, the saturated sterol that occurs in the endosperm of maize and wheat. That the alcoholic hydroxyl has not been changed was shown by the preparation of an *acetyl* derivative, $C_{27}H_{47}OAc$, m. p. 138—139°. A. C.

Separation of Unsaturated from Saturated Sterols. R. J. ANDERSON and F. P. NABENHAUER (*J. Amer. Chem. Soc.*, 1924, **46**, 1957—1960).—A mixture of sitosterol and dihydrositosterol can be almost completely separated by fractional crystallisation from alcohol, in which the latter is less soluble, if sufficient material is available. It is, however, impossible to remove the last traces of sitosterol in this way. Only the sitosterol takes up bromine, but an attempt to separate a brominated mixture of the acetyl derivatives was equally ineffective. A modification of the Liebermann–Burchard reaction (cf. A., 1885, 1075) gave satisfactory results in one operation. The mixed sterols are dissolved in carbon tetrachloride and the solution is mixed with acetic anhydride; concentrated sulphuric acid is then added while the mixture is shaken and cooled. On adding a little water and keeping the mixture, the acids form a purple upper layer containing the unsaturated sterol in solution. The saturated sterol remains dissolved in the lower carbon tetrachloride layer, partly as acetyl compound and partly as an ethereal sulphate. After distilling off the solvent, the residue is hydrolysed by means of alcoholic potassium hydroxide and yields the dihydrositosterol in a pure condition. The intensely coloured acid mixture contains the unsaturated sterol in a very stable chemical combination. On dilution with water, the colour becomes grass-green, and on neutralisation with alkali, a clear yellow. This reaction product has not been isolated in the pure form. A. C.

***k*-[Kombe-]Strophanthidin.** H. THOMS and F. UNGER (*Z. angew. Chem.*, 1924, **37**, 721—723).—Chiefly a critical bibliographical survey (cf. Jacobs, this vol., i, 65, 67; Brauns and Closson, A., 1915, i, 435, etc.). The compound has the formula $C_{23}H_{32}O_6,\frac{1}{2}H_2O$. Its *methyl ether* has m. p. 229—230°, decomp. 232—234°. Its phenylhydrazone has a higher m. p., viz., 242—243°, than that

recorded by Jacobs and Heidelberger (A., 1923, i, 123). *Dibromostrophanthidin*, $C_{23}H_{32}Br_2O_6$, has m. p. 154·5°. Other observations are briefly described. W. A. S.

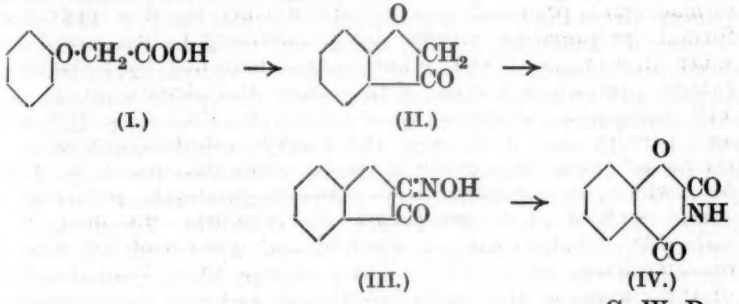
Constitution of Catechin. VI. Production of Maclurin from Acacatechin. E. O. HAZLETON and M. NIERENSTEIN (*J. Amer. Chem. Soc.*, 1924, **46**, 2100—2105).—By the action of *Penicillium solitum* on a 0·72% solution of acacatechin in water containing 5% of sucrose, a yield of 86% of the theoretical amount of maclurin is produced, an observation which is not consistent with formulæ proposed for catechin by Freudenberg, Ortner, and Fikentscher (this vol., i, 660). The phenol obtained by reduction of catechin tetramethyl ether with sodium and alcohol (cf. T., 1920, **117**, 1156) which Freudenberg and Cohn (A., 1923, i, 1219) regarded as 2-hydroxy-4 : 6 : 3′ : 4′-tetramethoxy-αγ-diphenylpropane, on ethylation with ethyl iodide gives an *ethoxy* derivative, m. p. 49—50°, which on oxidation with alkaline potassium permanganate yields 4 : 6 : 3′ : 4′-*tetramethoxy-2-ethoxydiphenylacetic acid*, m. p. 137—138° (*methyl* ester, obtained by methylation of the acid with diazomethane, m. p. 64°). These results show that the fission of the chromane nucleus in acacatechin leads to the formation of an αα-diphenylpropane derivative in accordance with the structure assigned to acacatechin by Nierenstein, and not to the αγ-derivative claimed by Freudenberg and Cohn. R. B.

Oak-wood Tannin. Preparation and Purification of Tannins. I. K. FEIST and H. BESTEHORN (*Arch. Pharm.*, 1924, **262**, 291—304).—Oak-wood tannin is best extracted by the method of Feist and Haun (A., 1914, i, 195), with the modification that a mixture of alcohol and acetone is used for the final extraction. The crude tannin thus obtained contains about 9% of inorganic matter, notably calcium, and 5 to 30% of ellagic acid. The latter cannot be removed by crystallisation or dialysis from pyridine; a solution of the crude tannin dissolves ellagic acid to the extent of about 26% of its tannin content. The inorganic matter, but not the ellagic acid, may be completely removed by an electro-osmotic method. The purified tannin yielded a methyl derivative of molecular weight 1343. Attempts to purify the crude tannin by ultra-filtration failed. B. F.

Tetrahydrofurfuraldehyde. H. SCHEIBLER, F. SOTSCHECK, and H. FRIESSE (*Ber.*, 1924, **57**, [*B*], 1443—1448).—Furfuraldehyde diacetate, b. p. 129°/17 mm., m. p. (plates) 52—53°, m. p. (needles) 49—51° (cf. Law, A., 1908, i, 321), is hydrogenated in ethereal solution in the presence of palladised charcoal to *tetrahydrofurfuraldehyde diacetate*, b. p. 133°/29 mm., d_4^{20} 1·1495, $n_D^{20·3}$ 1·44052. It is hydrolysed by *N*-sulphuric acid to *tetrahydrofurfuraldehyde*, a colourless, mobile liquid, b. p. 45—47°/29 mm., 142—143°/779 mm., d_4^{20} 1·0501, $n_D^{20·6}$ 1·47036; the non-crystalline *phenylhydrazone* and *oxime* and the crystalline as.-*phenylbenzylhydrazone*, m. p. 67°, are described. Furfuraldehydediethylacetal prepared by Claisen's method from furfuraldehyde and ethyl orthoformate (cf. A., 1907,

i, 940) is unsuitable for the preparation of tetrahydrofurfuraldehyde since it contains unchanged aldehyde. H. W.

Transformation of Furan Rings into Oxazine Rings. E. MAMELI (*Atti I. Congr. naz. Chim. pur. appl.*, 1923, 436; from *Chem. Zentr.*, 1924, i, 2517; cf. A., 1923, i, 61).—2 : 4-*Diketobenzisooxazine* (IV) has been prepared from phenol by way of the compounds I—III. The corresponding methyl derivatives have been prepared from *o*- and *p*-cresol.



(I.) (II.) (III.) (IV.)

G. W. R.

Formation of Coumaranones, Chromanones, and Hydroxyhydrindones from Phenols. K. VON AUWERS (*Annalen*, 1924, 439, 132—175; cf. A., 1920, i, 392, 866; 1921, i, 464; 1922, i, 1192). **I. Dicyclic Ketones from *p*-Cresol and α-Bromo-α-ethylbutyric Acid** [with T. MEISSNER.]—*α-Bromo-α-ethylbutyryl bromide*, b. p. 94°/20 mm., reacts with *p*-tolyl methyl ether in carbon disulphide solution in presence of aluminium chloride to yield o-[*α-bromo-α-ethyl-butyryl*]-p-*cresol*, b. p. 175°/14 mm., d_4^{20} 1·307, n_{He}^{20} 1·5654. This is converted by cold sodium hydroxide into a mixture of about 2 parts of o(*α-hydroxy-α-ethylbutyryl*)-p-*cresol*, m. p. 43—44°, b. p. 166—168°/18 mm., d_4^{20} (supercooled) 1·081, n_{He}^{20} 1·5409 (*semicarbazone*, m. p. 180—181°), and 1 part of 5-*methyl*-2 : 2-*diethylcoumaranone*, b. p. 145—146°/15 mm., d_4^{20} 1·034, n_{He}^{20} 1·5326. The latter is the chief product of the reaction at 100°, and in behaving in this way the diethyl compound differs sharply from the dimethyl analogue (*loc. cit.*). When the bromobutyryl-*p*-cresol is heated with diethylaniline, 2 : 6-*dimethyl*-3-*ethylchromanone*, b. p. 151—153°, d_4^{21} 1·0627, n_{He}^{21} 1·53912 (*semicarbazone*, m. p. 210—211°; p-*nitrophenylhydrazone*, red prisms, m. p. 207—209°) is obtained; this yields a 2 : 3-*dibromo* derivative, m. p. 119—120°, and, by less prolonged treatment, a 3-*bromo* derivative, an oil, which when heated with diethylaniline gives 2 : 6-*dimethyl*-3-*ethylchromanone*, a yellow oil, b. p. 168—173°/13 mm., d_4^{20} 1·092, n_{He}^{20} 1·5540; the latter is also obtained by treating a mixture of ethyl ethylacetoacetate and *p*-cresol with phosphorus pentoxide. Only a little dimethylethylchromanone is obtained from *p*-tolyl methyl ether, α-ethylcrotonyl chloride, and aluminium chloride, the chief product being o-*butyryl*-p-*cresol*, m. p. 32—33°, b. p. 132—133°/15 mm., $d_4^{56·2}$ 1·0191, $n_{He}^{56·2}$ 1·5240 (p-*nitrophenylhydrazone*, red prisms,

m. p. 184—186°; with semicarbazide two *compounds*, m. p. 190° and 159—162°, respectively, were obtained). A comparison sample was prepared by treating p-*tolyl* n-*butyrate*, b. p. 140—141°, with aluminium chloride. p-*Tolyl* α-*bromo*-α-*ethylbutyrate* has b. p. 167—168° and when treated with aluminium chloride gives the above 2 : 6-dimethyl-3-ethylcoumaranone, together with 7-*hydroxy*-3 : 4-*dimethyl*-2-*ethylhydrindone*, b. p. 149·6—150·2°/8·5 mm., d_4^{20} 1·073, n_{He}^{20} 1·5484 (*semicarbazone*, m. p. 186—188°; p-*nitrophenylhydrazone*, orange-red prisms, m. p. 218—219°). p-*Tolyl* α-*ethylcrotonate* (from the cresol and the acid chloride) has b. p. 144—146°/12 mm., d_4^{20} 1·009, n_{He}^{20} 1·5132, and is converted by treatment with aluminium chloride at 130—140° into the above hydroxyhydrindone. Anisole and crotonyl chloride in carbon disulphide solution react with aluminium chloride to give p-*crotonylanisole*, m. p. 22°, b. p. 165—167°/15 mm., $d_4^{11·7}$ 1·0906, $n_{He}^{11·7}$ 1·58723, the *dibromide* of which has m. p. 104·5—105·5°. 7-Hydroxyhydrindone has b. p. 128—130·5°/9·5 mm.; 7-hydroxy-2 : 4-dimethylhydrindone has b. p. 136·5—137·5°/8 mm., $d_4^{63·8}$ 1·0890, $n_{He}^{63·8}$ 1·54501; 7-hydroxy-3 : 4-dimethylhydrindone has b. p. 140·3°/8 mm., $d_4^{63·8}$ 1·0999, $n_{He}^{63·8}$ 1·55156. The refractivities for the α, β, and γ lines are also recorded and the relations between the optical properties and the constitutions of the above compounds are discussed.

II. Dicyclic Ketones from *m*-Cresol and α-Bromo*iso*butyric Acid [with J. Koch.]—o-(α-Bromo*iso*butyryl)*p*-cresol does not yield a coumaranone, but the corresponding derivative of *s-m*-xylenol readily undergoes this conversion (*loc. cit.*). It is now shown that the reaction is governed by the position of the methyl group or groups in the phenyl nucleus. Thus, when *m*-tolyl methyl ether and α-bromo*iso*butyryl bromide are treated in carbon disulphide with aluminium chloride a product is obtained from which may be separated 4(α-chloro- or α-bromo-*iso*butyryl)-*m*-cresol, 7-hydroxy-2 : 5-dimethylhydrindone, 5-hydroxy-2 : 7-dimethylhydrindone, and 2 : 2 : 4-trimethylcoumaranone; these substances were identified by comparing them with samples prepared in other ways (see below). When less aluminium chloride was used 4-(α-hydroxy*iso*butyryl)*m*-cresol also was eventually obtained. m-*Tolyl*-α-*bromo*isobutyrate (from the cresol and the acid chloride), b. p. 132—135°/11 mm., when heated at 140° with aluminium chloride yields 7-*hydroxy*-2 : 5-*dimethylhydrindone*, a pale yellow, steam-volatile oil, b. p. 138—139°/11 mm., d_4^{20} 1·119 or 1·123, n_{He}^{20} 1·5672 or 1·5647 (*semicarbazone*, needles, m. p. 232—233°; *phenylhydrazone*, m. p. 122—123°) and 5-*hydroxy*-2 : 7-*dimethylhydrindone* (not volatile in steam), m. p. 190—191°, b. p. 220°/10 mm. (*semicarbazone*, m. p. 228—229°; *acetyl* compound, m. p. 70—71°; 2 : 4 : 6-*tribromo* derivative, m. p. 169—170°). 2 : 2 : 4-*Trimethylcoumaranone* has m. p. 54—55°, b. p. 108°/10 mm., and yields the 5 : 7-*dibromo* derivative (m. p. 114°) when treated with an excess of bromine and a little aluminium. m-*Tolyl* iso*butyrate*, b. p. 104—106°/11 mm., when heated at 100° with aluminium chloride yields 4-iso*butyryl*-m-*cresol*, b. p. 120—121°/11 mm., d_4^{20} 1·042, n_{He}^{20} 1·5401, which, brominated, affords 6-*bromo*-4-(α-*bromo*iso*butyryl*)m-*cresol*, m. p. 98—99°, and 2 : 6-*di*-

bromo-4-(α-*bromoisobutyryl*)m-*cresol*, m. p. 90—92°. The latter is oxidised by hydrogen peroxide to 4 : 6-dibromo-*m*-hydroxytoluic acid. *m*-Tolyl methyl ether and α-bromopropionyl bromide yield chiefly the steam-volatile 4-(α-*chloropropionyl*)m-*cresol*, b. p. 145—147°/13 mm., which, when heated with sodium acetate and alcohol, is converted into 2 : 6-*dimethylcoumaranone*, m. p. 60—61°, b. p. 118—120°/13 mm.; the *semicarbazone*, m. p. 204—205°, was produced normally at the ordinary temperature, but at 40—50° the product was the *disemicarbazone* of 4-*pyruvyl*-m-*cresol*, which crystallises with 1 mol. H_2O and has m. p. 245°; with *p*-nitrophenylhydrazine the *dinitro-osazone* of this compound, m. p. 261°, or 275° when anhydrous, was obtained. When 2 : 6-dimethylcoumaranone is treated with sodamide and methyl iodide, 2 : 2 : 6-*trimethylcoumaranone*, m. p. 52°, b. p. 108°/12 mm. (*semicarbazone*, m. p. 250°; p-*nitrophenylhydrazone*, m. p. 196°), is obtained. When the crude steam-volatile product of the condensation of *m*-tolyl methyl ether and α-bromo*iso*butyryl bromide is shaken with cold dilute sodium hydroxide, a mixture is obtained from which may be separated 7-hydroxy-2 : 5-dimethylhydrindone, 2 : 2 : 4-trimethylcoumaranone, and 4-(α-*hydroxyisobutyryl*)m-*cresol*, m. p. 54—55° (*semicarbazone*, m. p. 154—156°; *acetyl* derivative, m. p. 56—57°, b. p. 183—185°/13 mm.); but if the oil be heated with diethylaniline a chief product is 3 : 7-*dimethylchromanone*, m. p. 55—56° (*semicarbazone*, m. p. 221°). This compound is obtained also from *m*-tolyl methyl ether and β-chloro*iso*butyryl chloride; it yields a 3-*bromo* derivative, m. p. 97—98°, which, when heated with diethylaniline, affords 3 : 7-*dimethylchromone*, m. p. 78—79°, and the latter is disrupted by boiling sodium ethoxide, giving 4-propionyl-*m*-cresol, identified as semicarbazone (see below). m-*Tolyl propionate*, b. p. 108—110°/10 mm., when treated with aluminium chloride at 100°, yields the steam-volatile 4-*propionyl*-m-*cresol*, m. p. 41·5—42·5°, b. p. 115—120°/10 mm. (*semicarbazone*, m. p. 206—208°), and 6-*propionyl*-m-*cresol*, m. p. 114—115° (*semicarbazone*, m. p. 152·5—153·5°). 2 : 6-*Dibromo*-m-*tolyl methyl ether* has m. p. 73—74°. W. A. S.

Transformation of *o*-Hydroxychalkone into Flavanone. Dehydrogenation of Flavanone to Flavone by Phosphorus Pentachloride. Synthesis of Flavone. A. Löwenbein (*Ber.*, 1924, **57**, [*B*], 1515—1516).—Flavanone is readily obtained in 80% yield by the addition of excess of aqueous sodium hydroxide (1—2%) to a warm, alcoholic solution of *o*-hydroxyphenyl styryl ketone. It is converted by phosphorus pentachloride in the presence of boiling benzene into hydrogen chloride and a yellow, additive compound of flavone and phosphorus pentachloride from which the former is obtained in 80% yield by the action of alcohol. H. W.

2 : 4-Diarylchromenes. A. Löwenbein [with E. Pongrácz and E. A. Spiess] (*Ber.*, 1924, **57**, [*B*], 1517—1526).—Phenyl *o*-hydroxystyryl ketone is converted by an ethereal solution of magnesium phenyl bromide into 2 : 4-*diphenylchroman*-2-*ol*,

$C_6H_4<\begin{matrix}CHPh\cdot CH_2\\ O---CPh\cdot OH\end{matrix}$, m. p. 165—166°, which is dehydrated by boiling glacial acetic acid to 2 : 4-*diphenyl*-Δ^2-*chromene*,

$$C_6H_4<\begin{matrix}CHPh\cdot CH\\ O---CPh\end{matrix}$$

m. p. 110°. The phenyl groups in these compounds are attached to different carbon atoms, and hence addition of the Grignard reagent to the unsaturated ketone occurs at the terminal points of the conjugated system, since phenyl *o*-hydroxystyryl ketone and magnesium *p*-tolyl bromide yield 2-*phenyl*-4-p-*tolylchroman*-2-*ol*, m. p. 141° (2-*phenyl*-4-p-*tolyl*-Δ^2-*chromene*, m. p. 85°), whereas magnesium phenyl bromide and *p*-tolyl *o*-hydroxystyryl ketone yield 4-*phenyl*-2-p-*tolylchroman*-2-*ol*, m. p. 160° (4-*phenyl*-2-p-*tolyl*-Δ^2-*chromene*, m. p. 137°). The constitution of the diphenylchromene is further confirmed indirectly, since it differs from 2 : 4-*diphenyl*-Δ^3-*chromene*, $C_6H_4<\begin{matrix}CPh{:}CH\\ O---CHPh\end{matrix}$, m. p. 106°, obtained by dehydration of 2 : 4-*diphenylchroman*-4-*ol*, m. p. 112°; the structure of the latter compound is placed beyond doubt by its production from magnesium phenyl bromide and flavanol. The two isomeric 2 : 4-diphenylchromenes are oxidised by ferric chloride to the same 2 : 4-diphenylbenzopyrylium salts (*perchlorate*, m. p. 217—218°; *additive* compound of the chloride and ferric chloride, m. p. 168°).

Coumarin is converted by magnesium phenyl bromide in the presence of a mixture of ether and benzene into a mixture of 2 : 4-diphenylchroman-2-ol [identical with the product from phenyl *o*-styryl ketone described above and erroneously considered by Houben (A., 1904, i, 334) to be diphenyl-*o*-hydroxystyrylcarbinol] and 2 : 2-*diphenyl*-Δ^3-*chromene*, $C_6H_4<\begin{matrix}CH{:}CH\\ O---CPh_2\end{matrix}$, m. p. 93°. The latter substance appears to be formed from coumarin without rupture of the lactone ring; it is converted by boiling glacial acetic acid or alcoholic hydrogen chloride into the *compound*, $C_6H_4<\begin{matrix}CH\\ O\end{matrix}>C\cdot CHPh_2$ or $C_6H_4<\begin{matrix}CH_2\\ O\end{matrix}>C{:}CPh_2$, m. p. 239°, presumably after hydrolysis to the allene derivative,

$$OH\cdot C_6H_4\cdot CH{:}C\cdot CPh_2.$$

Magnesium α-naphthyl bromide and coumarin yield 2 : 4-*di*-α-*naphthylchroman*-2-*ol*, m. p. 156°, which is converted by boiling glacial acetic acid into 2 : 4-*di*-α-*naphthyl*-Δ^2-*chromene*, m. p. 137°. The following compounds are derived from magnesium phenyl bromide and the requisite methylcoumarin: 5 : 7-*dimethyl*-2 : 4-*diphenylchroman*-2-*ol*, m. p. 111°, which yields 5 : 7-*dimethyl*-2 : 4-*diphenyl*-Δ^2-*chromene*, m. p. 118°; 4 : 6-*dimethyl*-2 : 4-*diphenylchroman*-2-*ol*, m. p. 110°, and thence 4 : 6-*dimethyl*-2 : 4-*diphenyl*-Δ^2-*chromene*, m. p. 127°; 4 : 7-*dimethyl*-2 : 4-*diphenylchroman*-2-*ol*, m. p. 144°, which yields 4 : 7-*dimethyl*-2 : 4-*diphenyl*-Δ^2-*chromene*, m. p. 86°.

[With L. Popper.]—Phenyl *o*-hydroxystyryl ketone is converted by hydrogen chloride in the presence of ether into 2-*phenylbenzo*-

pyrylium chloride, $C_{15}H_{11}OCl,HCl$, m. p. 85—86° (decomp.); the corresponding *perchlorate* has m. p. 186—187°. Either salt is converted by magnesium phenyl bromide into 2 : 4-diphenyl-Δ^2-chromene. H. W.

Preparation of Dehydracetic Acid from Ethyl Acetoacetate and the Mechanism of the Reaction. F. Arndt and P. Nachtwey (*Ber.*, 1924, **57**, [*B*], 1489—1491).—Dehydracetic acid is prepared in 86% yield by protracted ebullition of ethyl acetoacetate under a reflux condenser so regulated that the liberated ethyl alcohol escapes. Since dehydracetic acid is not converted by alcohol under these conditions into ethyl acetoacetate, the usual equilibrium in the decomposition of the latter depends on the action of alcohol on some intermediate product, probably the compound $COMe\cdot CH_2\cdot CO\cdot O\cdot CMe\cdot CH\cdot CO_2Et$. H. W.

Aconite Alkaloids. I. Different Isomerides of Japaconitine. R. Majima, H. Suginomé, and S. Morio (*Ber.*, 1924, **57**, [*B*], 1456—1466).—The dried tubers of various species of Japanese *Aconitum* are mixed with calcium carbonate and extracted with alcohol (95%). The alcohol is removed as completely as possible, the residue is diluted with water, extracted with light petroleum, and treated with sodium carbonate solution, whereby crude japaconitine is partly precipitated, the remainder being obtained by extraction with chloroform. The crude alkaloid is extracted with ether and the soluble portion dissolved in hydrochloric acid; the solution is fractionally precipitated with sodium carbonate. The separate fractions are converted into their hydrobromides. Japaconitines of which the hydrobromides are readily crystallised from water are termed japaconitine-*A*, whereas the suffixes -*B* and -*C* denote the alkaloids of which the hydrobromides are respectively crystallisable from a mixture of alcohol and ether or not crystallisable from this mixture or water. In various species of Japanese *Aconitum* there are found isomeric alkaloids the hydrobromides of which fall within these classes; they are designated japaconitine -A_1, -B_1, and -C_1.

The following individual substances are described, certain of which have been examined previously by Dunstan and Read (T., 1900, **77**, 45) and Makoshi (A., 1909, i, 669). The temperatures of decomposition depend greatly on the mode of heating and are determined with reference to japaconitine-*A* or its hydrobromide. The method of "mixed melting points" fails in this series. The following compounds are described: Japaconitine-*A*, $C_{34}H_{47}O_{11}N$, decomp. 202—203°, $[\alpha]_D^{13}$ +20·7° in chloroform [hydrochloride (+3·5H_2O), decomp. 160—161°; (anhydrous), decomp. 165—166°; $[\alpha]_D^{18}$ −31·3° in water; hydrobromide (+4·5H_2O), decomp. 155—156°; (anhydrous), decomp. 172—173°; hydriodide, decomp. 205—209°; chloroaurate, decomp. 159—160°; triacetyl derivative, decomp. 191—193°; *perchlorate* (+H_2O), decomp. (anhydrous), 215—218°)]. *Japaconitine*-A_1, $C_{34}H_{47}O_{11}N$, decomp. 208—209°, $[\alpha]_D^{12}$ +26·4° in chloroform [*hydrobromide* (+3·5H_2O), decomp.

(anhydrous), 172—173°, $[\alpha]_D^{16}$ −22·5° in water; *chloroaurate*, decomp. 223—224°; *perchlorate*, decomp. 215—218°]. *Japaconitine*-B, $C_{34}H_{47}O_{11}N$, decomp. 208—209°, $[\alpha]_D^{11}$ +26·9° in chloroform [*hydrochloride*, decomp. 108—109°, $[\alpha]_D^{18}$ −24·7° in water; *hydrobromide* (+H_2O), decomp. 179·5—180·5°, $[\alpha]_D^{30}$ −21·8° in water; *hydriodide*, decomp. 228—231°; *chloroaurate*, decomp. 235—237°; *perchlorate*, decomp. 215—218°; *triacetyl* derivative, decomp. 196—197°]. *Japaconitine*-B_1, prisms, decomp. 194—195°, $[\alpha]_D$ +22·0° in chloroform (*chloroaurate*, decomp. 248—249°). *Japaconitine*-C, $C_{34}H_{47}O_{11}N$, prisms, decomp. 195—196°, $[\alpha]_D^{12}$ +18·3° in chloroform [*chloroaurate*, decomp. 243—245°; *perchlorate* (+2·5H_2O), decomp. (anhydrous), 175—178°]; *Japaconitine*-C_1, prisms, decomp. 193—195°, $[\alpha]_D$ +23·2° in chloroform (*chloroaurate*, decomp. 248—249°).

Japaconitine-*A* is hydrolysed in the presence of aqueous sulphuric acid to acetic acid and *japbenzaconine*-A, which is isolated as the hydrochloride (+2H_2O), decomp. 244—245°, $[\alpha]_D^{18}$ −29·8° in aqueous solution, decomp. (anhydrous) 265—266°, and by water at 160—170° to benzoic acid and japaconine-*A* (*hydrochloride*, $C_{25}H_{41}O_3N$,HCl,1·5H_2O, decomp. 173—175°; tetra-acetyl derivative, decomp. 235—236°, $[\alpha]_D^{18}$ −28·9° in chloroform). Similarly, japaconitine-*B* yields *japbenzaconine*-B *hydrochloride*, $C_{34}H_{45}O_{11}N$,HCl,H_2O, decomp. 251—252°, $[\alpha]_D^{18}$ −24·4° in aqueous solution and japaconine-*B* which is isolated as the very hygroscopic *hydrochloride* and the *tetra-acetyl* derivative, $C_{33}H_{49}O_{13}N$, decomp. 228—229°, $[\alpha]_D^{19}$ −19·1° in alcohol. H. W.

Aconite Alkaloids. II. Aconitine and Pyraconitine. R. Majima and H. Suginomé (*Ber.*, 1924, **57**, [*B*], 1466—1471).—The recognition of japaconitine as a mixture of isomerides (preceding abstract) has induced an examination of aconitine along similar lines whereby it also is found to be non-homogeneous.

Aconitine (Merck, ex *Aconito Napello*) is separated by aqueous hydrobromic acid into the readily crystallisable *aconitine*-A *hydrobromide*, decomp. 206—207°, and the amorphous *aconitine*-C *hydrobromide* (for use of suffixes, *A* and *C*, see preceding abstract). *Aconitine*-A, $C_{34}H_{47}O_{11}N$, forms hexagonal plates, decomp. 202—203°, $[\alpha]_D^{14}$ −18·1° in chloroform (*chloroaurate*, m. p. 151—152°). It is hydrolysed to *aconine*-A *hydrochloride*, $C_{25}H_{41}O_9N$,HCl,2H_2O, decomp. 169—170°, $[\alpha]_D^{9}$ −3·7° in water. *Tetra-acetylaconine*-A decomposes at 241—242°. *Aconitine*-C, $C_{34}H_{47}O_{11}N$, forms prismatic crystals, decomp. 203—204°, $[\alpha]_D^{10}$ −23·4° in chloroform (*chloroaurate*, decomp. 238—239°). It is hydrolysed to aconine-*C*, which is identified as the *tetra-acetyl* compound, decomp. 223—224°.

Thermal decomposition of japaconitine-*A* (cf. Schulze and Liebner, A., 1913, i, 1375; 1917, i, 470) yields two isomeric pyrojapaconitines designated α and β. Non-crystalline *pyrojapaconitine*-α gives a *hydrobromide*, $C_{32}H_{43}O_9N$,HBr, crystallisable from water, decomp. 262°, $[\alpha]_D^{13}$ −43·5° in water, a *perchlorate*, decomp. 252—254°, and a *chloroaurate* (+0·5H_2O), decomp. 143°. *Pyrojapaco-*

nitine-β could not be caused to crystallise; it yields a *hydrobromide*, $C_{32}H_{43}O_9N,HBr,2H_2O$, decomp. 226°, $[\alpha]_D^{24}$ −68·4° in water, a *perchlorate*, decomp. 286° after darkening at 276°, and a *chloroaurate* (+H_2O), decomp. 176—177°. Similarly, japaconitine-*B* yields two pyrojapaconitines, one of which is identical with pyrojapaconitine-β from japaconitine-*A*. The other, termed *pyrojapaconitine*-γ, forms prismatic crystals, decomp. 169—170°, $[\alpha]_D^{26}$ −108·4° in alcohol (*hydrobromide*, $C_{32}H_{43}O_9N,HBr,2H_2O$, decomp. 240—241°, $[\alpha]_D^{25}$ −105·4° in water; *perchlorate*, decomp. 270—271°; *chloroaurate*, decomp. 202°).

Aconitine-*A* in similar manner yields two pyraconitines (α and β) in the approximate ratio 3 : 1. The α-compound resembles closely pyrojapaconitine-α, with which it is possibly identical. The following salts of pyraconitine-α are described: *hydrobromide*, $C_{32}H_{43}O_9N,HBr$, decomp. 262°, $[\alpha]_D^{15}$ −42·7° in water; *perchlorate*, decomp. 254—256°; *chloroaurate* (+0·5H_2O), decomp. 143—144°. Pyraconitine-β yields a *hydrobromide*, $C_{32}H_{43}O_9N,HBr,3H_2O$, decomp. 207—208°, $[\alpha]_D^{17}$ −39·2° in water, a *perchlorate*, decomp. *ca.* 282—283°, and a *chloroaurate* (+H_2O), decomp. 191—192°. One of the two isomeric pyraconitines obtained from aconitine-*C* is identical with pyraconitine-β; the other, *pyraconitine*-γ, gives a non-crystalline hydrobromide and perchlorate and a *chloroaurate*, $C_{32}H_{43}O_9N,HCl,AuCl_3,H_2O$, decomp. 213—214°. H. W.

Aconite Alkaloids. III. So-called Jesaconitine. R. Majima and S. Morio (*Ber.*, 1924, **57**, [*B*], 1472—1476).—Examination of aconitum tubers grown in the region north of Tokyo discloses the presence of only two alkaloids, acetylanisoylaconine (which it is proposed to designate "jesaconitine") and japaconitine-A_2; the crude material is thus a less involved mixture than that derived from the aconitum grown in the south of Tokyo (this vol., i, 1223). The jesaconitine isolated by Makoshi (A., 1909, i, 669) from tubers grown in a similar neighbourhood and considered by him to be benzoylanisoylaconine appears to have suffered partial degradation before examination.

The extraction of the alkaloid and the separation of it into its components is effected in the manner described for japaconitine. *Jesaconitine*, decomp. 128—131°, gives a *perchlorate*, $C_{35}H_{49}O_{12}N,HClO_4$, decomp. 230—232°, $[\alpha]_D$ −16·7° in methyl-alcoholic solution, a *chloroaurate*, decomp. 208—209°, and a *perbromide*, decomp. 181—182°. When boiled with water containing the equivalent quantity of sulphuric acid, it yields jesoanisaconine (*hydrochloride*, $C_{33}H_{47}O_{11}N,HCl,3H_2O$, decomp. 209—210°, $[\alpha]_D^{20}$ −19·2° in water) and acetic acid. Hydrolysis with water at 160—170° converts it into acetic and *p*-anisic acids and jesaconine, which is found identical with aconine-*A*. Thermal decomposition of jesaconitine appears to yield a single pyrojesaconitine, which is isolated as the *perchlorate*, anhydrous prisms, decomp. 271—273°, $[\alpha]_D^{13}$ −27·4° in methyl alcohol.

Japaconitine-A_2, $C_{34}H_{47}O_{11}N$, decomp. 199—201°, $[\alpha]_D^{13}$ +18·7°

in chloroform, yields a *hydrobromide*, decomp. 172—173°, a *chloroaurate*, decomp. 143—144°, and a *perchlorate* ($+1{\cdot}5H_2O$), decomp. 214—216°, $[\alpha]_D^{13}$ −18·8° in methyl-alcoholic solution. It is hydrolysed to acetic and benzoic acids and japaconine-A_2 which is identical with aconine-*A*. When heated it yields pyrojapaconitine-α (hydrobromide, $C_{32}H_{43}O_9N$,HBr, decomp. 261—262°, $[\alpha]_D^{19}$ −42·0° in water; perchlorate, decomp. 250—254°; chloroaurate, decomp. 140—142°), which is probably identical with pyrojapaconitine-α and pyraconitine-α. H. W.

Mydriatic Alkaloids from the *Datura* Species. I. S. Osada (*Arch. Pharm.*, 1924, **262**, 277—291; cf. T., 1908, **93**, 2077).—The author proposes to investigate the structure of meteloidine, and reviews the literature dealing with teloidine and meteloidine, and the connexion of the former with tropine and scopoline. *Datura meteloides* is the only plant of the *Datura* species found to contain meteloidine, scopolamine and hyoscyamine being also present. The green- and violet-stalked varieties of *Datura alba*, Nees, each contained scopolamine, hyoscyamine, and atropine. Figures are given for the percentages of the different substances in various parts of the plants. B. F.

Angostura Alkaloids. I. Synthesis of Cusparine. E. Späth and O. Brunner (*Ber.*, 1924, **57**, [*B*], 1243—1251).—The synthesis of 7-methoxy-4-β-3′ : 4′-dimethoxyphenylethylquinoline and of the corresponding 2-β-3′ : 4′-dimethoxyphenylethyl compound and their non-identity with galipine disproves the constitution assigned to the latter by Troeger (A., 1913, i, 748; 1915, i, 447; 1921, i, 121). The key to the structure of cusparine and galipine is furnished by the observation that Troeger's acid, $C_{11}H_9O_3N$, is almost certainly 4-methoxyquinoline-2-carboxylic acid. Thence 4-methoxy-β-3′ : 4′-methylenedioxyphenylethylquinoline is synthesised and found identical with cusparine.

2-*Hydroxy*-7-*methoxy*-4-*methylquinoline*, m. p. 205—206° (the *hydrochloride* is described), prepared from *m*-methoxyaniline and ethyl acetoacetate, is converted successively into 2-*chloro*-7-*methoxy*-4-*methylquinoline*, m. p. 112·5—113°, and 7-*methoxy*-4-*methylquinoline*, a pale yellow liquid [*picrate*, m. p. 223·5—224° (decomp.)]. The latter substance is converted by zinc chloride and 3 : 4-dimethoxybenzaldehyde into 7-*methoxy*-4-β-3′ : 4′-*dimethoxyphenyl*-Δ^{α}-*ethinylquinoline hydrochloride*, which is reduced by hydrogen in the presence of palladised charcoal to 7-*methoxy*-4-β-3′ : 4′-*dimethoxyphenylethylquinoline*, m. p. 126°. 4-*Hydroxy*-7-*methoxy*-2-*methylquinoline*, m. p. 252—253° [*hydrochloride*, m. p. 269° (decomp.)], is similarly transformed successively into 4-*chloro*-7-*methoxy*-2-*methylquinoline*, m. p. 81—82°, 7-*methoxy*-2-*methylquinoline*, a liquid [*picrate*, m. p. 217° (decomp.) after softening at 204°], 7-*methoxy*-2-β-3′ : 4′-*dimethoxyphenyl*-Δ^{α}-*ethinylquinoline hydrochloride* and 7-*methoxy*-2-β-3′ : 4′-*dimethoxyphenylethylquinoline*, m. p. 82·5—83°.

7-*Methoxyquinoline*, b. p. 143—145°/11 mm., prepared from

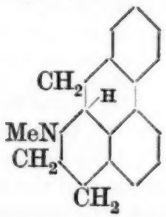
m-methoxyaniline, *p*-nitrophenol, glycerol, and concentrated sulphuric acid, is converted by benzoyl chloride and potassium cyanide and hydrolysis of the nitrile into *7-methoxyquinoline-2-carboxylic acid*, m. p. 154°. The base is converted by methyl sulphate and potassium cyanide and treatment of the product with potassium iodide into *4-cyano-7-methoxyquinoline methiodide*, m. p. 204—205° (decomp.), from which *4-cyano-7-methoxyquinoline*, m. p. 153—154°, is prepared in very poor yield. The nitrile is hydrolysed to *7-methoxyquinoline-4-carboxylic acid*, m. p. 273° (decomp.).

4-Methoxy-2-methylquinoline is converted by piperonal and anhydrous zinc chloride at 125° into *4-methoxy-2-β-3′ : 4′-methylenedioxyphenyl-Δ$^{\alpha}$-ethinylquinoline hydrochloride*, m. p. 193—195°, from which the corresponding *base* (dehydrocusparine), m. p. 186°, is isolated; the latter substance is reduced by hydrogen in the presence of palladised charcoal to 4-methoxy-2-β-3′ : 4′-methylenedioxyphenylethylquinoline, identical with natural cusparine.

H. W.

Chelidonium Alkaloids. III. J. GADAMER (with H. DIETERLE, [FRL.] A. STICHEL, M. THEYSSEN, and K. WINTERFELD) (*Arch. Pharm.*, 1924, **262**, 249—277; cf. A., 1920, i, 75, 872; 1921, i, 579).—This paper deals with the constitution of chelidonine. *d*-Chelidonine, $C_{20}H_{19}O_5N$, with cold acetic anhydride yields *d-O*-acetylchelidonine, m. p. 165—166°, $[\alpha]_D$ +110°. In the hot, however, 1 mol. of water is lost, optically inactive *N-acetylanhydrochelidonine*, $C_{22}H_{19}O_5N$, m. p. 152°, being formed. The nitrogen being originally tertiary, it is clear that a ring containing it has been opened and the loss of activity indicates that an asymmetrical carbon is probably involved in the reaction. On the ground of resemblances in this and other respects with the alkaloids of the so-called aporphine group (aporphine, I, is regarded as the parent

(I.)



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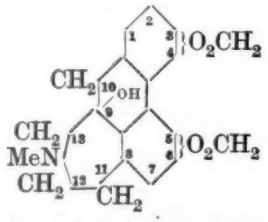
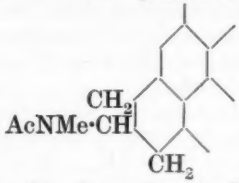
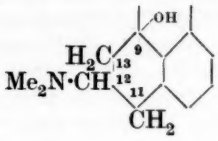


of the phenanthrene alkaloids, and its synthesis will be reported later) a formula for chelidonine has already been suggested (A., 1920, i, 75). This is now withdrawn, and replaced by the formula II, based on the reactions cited above, together with the view that in nature the substance may be formed from phenylacetaldehyde, *N*-methyl-β-phenylethylamine, and formaldehyde, for protopine and β-homochelidonine (*allo*cryptopine), may theoretically be decomposed into these component parts. The suggested formation in nature of chelidonine from these components is outlined. The formation of *N*-acetylanhydrochelidonine may be explained by fission of the ring between the nitrogen and C_{13}, re-closing of the

ring between C_{13} and C_{12}, and loss of water between C_{10} and the asymmetric atom C_9, giving (III).

(III.) 



(IV.)

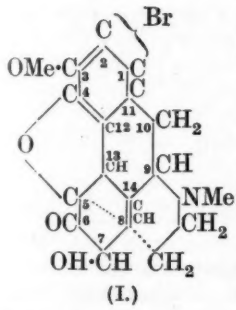
[With H. DIETERLE.]—When treated with methyl iodide, chelidonine first affords *chelidoninemethine*-A, $C_{21}H_{21}O_5N$, m. p. 145—146°, $[\alpha]_D$ −271·3° in chloroform (also formed by the action of methyl iodide on *O*-acetylchelidonine), and *chelidoninemethine*-B, m. p. 107—108°, $[\alpha]_D$ −100°, which occurs in the mother-liquor of the *A* methine as prepared by the first method. These two are regarded as stereoisomerides, and it is concluded that their formation is due to fission of the 7-ring and its reclosing, as in the case of the acetylation, so that the bases have formula IV. The existence of two stereoisomerides is due to the fact that a new asymmetric atom (12) has been superimposed on the original one (9). On further treatment with methyl iodide the *A* methine yields the corresponding *chelidoninemethinium methiodide*, $C_{22}H_{24}O_5NI$, m. p. 232—234° (decomp.), $[\alpha]_D$ −50°, which rapidly racemises in solution. The action of hot acetic anhydride on the *A* methine or its methiodide furnishes an optically inactive *substance*, $C_{21}H_{18}O_6$, m. p. 157—159° (the by-products being dimethylacetamide and trimethylamine respectively). The latter substance is an acetyl derivative, for on deacetylation by Schiff's method it yields a *substance*, $C_{19}H_{16}O_5$, m. p. 170—171°, resistant to oxidation. By the action of methyl sulphate on *O*-acetylchelidonine or chelidonine and subsequent treatment with sodium hydroxide there is formed optically inactive *methylanhydrochelidonine*, $C_{21}H_{19}O_4N$, m. p. 152—153°, probably by loss of water between C_9 and C_{10}; the same substance is formed by the action of methyl iodide on chelidonine under special conditions. Methylanhydrochelidonine forms a *methiodide*, $C_{22}H_{22}O_4NI$, m. p. 242—244°, which may be readily converted into the corresponding *methonitrate*, $C_{22}H_{22}O_6N_2$, m. p. 260—261°, and *methochloride*, m. p. 215—217°. On reduction with sodium amalgam, the latter yields trimethylamine and the *substance*, $C_{19}H_{14}O_4$, m. p. 244—245°, which is resistant towards permanganate, and is regarded as containing a phenanthrene nucleus. Methylanhydrochelidonine methiodide, on treatment with moist silver oxide, probably gives rise to the corresponding *hydroxide*; the latter, however, was not isolated, but immediately distilled under reduced pressure, when trimethylamine was evolved. *ψ-Anhydrochelidonine*, $C_{20}H_{17}O_4N$, m. p. 89—89·5°, was prepared from its *hydrochloride*, m. p. 204—205°, which results from the hydrolysis of *N*-acetylanhydrochelidonine with hydrochloric acid. Methyl iodide converts ψ-anhydrochelidonine into methylanhydrochelidonine methiodide, a *substance*, m. p. 133—134°, being formed as a by-product. In both methods of preparation of the *A* methine

there is formed as a by-product a *tertiary base*, m. p. 195—198°, $[\alpha]_D$ +83° (in 2% chloroform solution). As a by-product in the treatment of chelidonine with methyl sulphate, there is formed O-*methylchelidonine*, $C_{21}H_{21}O_5N$, m. p. 162—163°, $[\alpha]_D$ +186° (in 0·5% alcohol solution), converted on heating with acetic anhydride into *N*-acetylanhydrochelidonine.

For purposes of simplicity, the breaking of the 7-ring has been consistently regarded as occurring between the nitrogen and C_{13}; actually it may also occur between N and C_{12}, which would result in the possibility of a new set of formulæ. B. F.

Action of Reducing Agents on Bromocodeinone. E. SPEYER and K. SARRE (*Ber.*, 1924, **57**, [*B*], 1404—1409).—Bromocodeinone, prepared by a modification of Freund's method (A., 1906, i, 303), is reduced by hydrogen in acetic acid solution in the presence of palladised charcoal to dihydrocodeinone, identical with the product described by Freund and Speyer (A., 1921, i, 126) and by Mannich and Löwenheim (A., 1921, i, 125). When electrolytically reduced in sulphuric acid solution (25%) at lead electrodes, bromocodeinone yields *dihydrodeoxycodeine*, $2C_{18}H_{23}O_2N,EtOH$, decomp. 139—140°, $[\alpha]_D^{13}$ +58·15° in dilute acetic acid solution, the product being formed by the replacement of bromine by hydrogen, reduction of the 6-keto to the methylene group, and rupture of the oxygen bridge with formation of a hydroxy group. It yields a *salicylate*, m. p. 198°, a *methiodide*, m. p. 199°, and a methyl ether which is isolated as the *methiodide*, m. p. 245°. Concentrated potassium hydroxide solution transforms the latter substance into the non-crystalline demethyldihydrodeoxycodeine methyl ether (*hydriodide*, $C_{20}H_{27}O_2N,HI$, m. p. 220° after softening; *methiodide*, m. p. 103°). The latter substance loses trimethylamine when heated with potassium hydroxide, but the nitrogen-free product was too unstable to be isolated. Reduction of dihydrodeoxycodeine in the presence of colloidal palladium gives β-tetrahydrodeoxycodeine (cf. Freund, A., 1920, i, 759). H. W.

Action of Bromine on Hydroxycodeinone and Hydroxydihydrocodeinone. E. SPEYER and K. SARRE (*Ber.*, 1924, **57**, [*B*], 1409—1422).—Hydroxycodeinone hydrobromide (cf. Freund and Speyer, A., 1917, i, 217) dissolved in cold water is converted by bromine water into *bromohydroxycodeinone* (I), m. p. 204—205°, $[\alpha]_D^{13}$ −80·21° in acetic acid solution; the corresponding *hydrobromide*, decomp. 280° after softening, *acetyl* derivative, m. p. 238°, and *phenylhydrazone*, decomp. 250°, are described. The substance is converted by hydrogen in the presence of palladium into hydroxydihydrocodeine, m. p. 218—220°. If, however, hydroxycodeinone is brominated in boiling glacial acetic acid solution, a perbromide is produced which is transformed by alcohol into *dibromohydroxycodeinone*, m. p. 194—195°, $[\alpha]_D^{13}$ −120·4° in



(I.)

*t t**

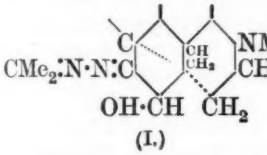
acetic acid solution; this substance gives a *hydrobromide*, decomp. 265°, an *acetyl* derivative, m. p. 219°, and a *phenylhydrazone*, decomp. 238°. It resists dehalogenation by the usual methods, but is converted by catalytic hydrogenation into hydroxydihydrocodeinone, m. p. 218—220°. Since it is also produced by the bromination of bromohydroxycodeinone in boiling glacial acetic acid, the primary action is considered to consist of addition of bromine at positions 8 and 14 (see I) followed by loss of hydrogen bromide, leaving the second bromine atom in position 8. Confirmation of this hypothesis is found in the observation that dibromohydroxycodeinone is converted by sodium hyposulphite [which has been observed previously (Freund and Speyer, *loc. cit.*) to effect saturation of the double bond between the carbon atoms 8 and 14] into *bromohydroxydihydrocodeinone*, m. p. 182° (*hydrobromide*, decomp. 227—230° after softening, $[\alpha]_D^{13}$ −93·15° in aqueous solution; *monoacetyl* derivative, m. p. 217°; *semicarbazone*, decomp. 249°). Bromohydroxydihydrocodeinone is also obtained by the action of bromine water on a cold, aqueous solution of hydroxydihydrocodeinone hydrobromide and by the action of sodium hyposulphite on bromohydroxycodeinone; it is converted by palladium and hydrogen into hydroxydihydrocodeinone.

The action of bromine on hydroxydihydrocodeinone dissolved in boiling glacial acetic acid yields a crystalline *perbromide* from which *tribromohydroxydihydrocodeinone*, $C_{18}H_{18}O_4NBr_3$, decomp. 228° after softening, $[\alpha]_D^{13}$ −225·56° in acetic acid solution, is prepared. The compound is also obtained by the bromination under similar conditions of bromohydroxydihydrocodeinone, into which it is reconverted by sodium hyposulphite. The bromine atoms are hence considered to occupy the positions 1 or 2, 8 and 14 (see I). It gives a *hydrobromide*, decomp. 255°, and an *acetyl* derivative, decomp. 220° after softening. The tribromo compound is converted by 2*N*-sodium hydroxide solution into a feebly basic *substance*, $C_{18}H_{20}O_6NBr,H_2O$, decomp. 302° after softening, which is regarded as bromo-7 : 8 : 14-trihydroxydihydrocodeinone; it yields, however, only a *monoacetate* ($+H_2O$), decomp. 267°. Dehalogenation by means of hydrogen and palladium yields 7 : 8 : 14-*trihydroxydihydrocodeinone*, decomp. 320° after softening, $[\alpha]_D^{13}$ −76·55° in feebly alkaline solution.

Hydroxycodeinone-*N*-oxide (cf. Freund and Speyer, *loc. cit.*) which has now been obtained in the crystalline form, decomp. 243°, is converted by acetic anhydride and sulphuric acid into "*ordinary*" *hydroxycodeinone*-N-*oxidesulphonic acid*, long rodlets, decomp. above 260°, and *α-hydroxycodeinone*-N-*oxidesulphonic acid*, rectangular leaflets, incipient decomp. 270°. The former acid is converted by sulphurous acid into *hydroxycodeinonesulphonic acid*, decomp. 310°. Attempts to replace the sulphonic group by bromine were unsuccessful. H. W.

Catalytic Hydrogenation of Hydroxycodeinone- and Hydroxydihydrocodeinone-hydrazones by Palladium and Hydrogen. E. Speyer and K. Sarre (*Ber.*, 1924, **57**, [*B*], 1422—1427).—Hydroxycodeinone is readily converted by hydrazine

hydrate into the corresponding *hydrazone*, m. p. 221—222°, which does not appear to yield the desired methylene derivative when heated with sodium ethoxide solution under pressure. Hydroxydihydrocodeinone and hydrazine hydrate in the presence of glacial acetic acid give *hydroxydihydrocodeinonehydrazone*, $C_{18}H_{23}O_3N_3$, m. p. 213—214° (slight decomp.); it is not reduced by hydrogen and palladium in dilute acetic acid solution. Under similar conditions, hydroxycodeinonehydrazone absorbs 2 mols. of hydrogen with production of ammonia and *hydroxydihydrocodeinoneketimine*, $C_{18}H_{22}O_3N_2$, m. p. 216—217° after softening, which is readily hydrolysed by acids to ammonia and hydroxydihydrocodeinone. If

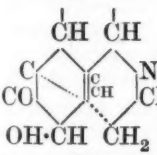


(I.)

hydrogenation is effected in the presence of aqueous acetone, only 1 mol. of hydrogen is absorbed and *hydroxydihydrocodeinonedimethylketazine* (I), m. p. 159°, is produced. Hydroxycodeinonehydrazone condenses with acetone in the presence of ammonia to give *hydroxycodeinonedimethylketazine*, m. p. 171°, which could not be hydrogenated satisfactorily to the dihydro compound described above.

H. W.

Action of Cyanogen Bromide on Hydroxycodeinone and Hydroxydihydrocodeinone. E. Speyer and K. Sarre (*Ber.*, 1924, **57**, [*B*], 1427—1430).—Hydroxycyanonorcodeinone (Freund and Speyer, A., 1917, i, 217) is converted by boiling sulphuric acid (25%) into *hydroxynorcodeinone* (cf. I), decomp. 218°, $[\alpha]_D^{13}$ −123·33° in dilute acetic acid solution. It yields a crystalline *hydrobromide* and a *nitroso* derivative, m. p. 234°. It is converted by sodium ethoxide and allyl bromide into the non-crystalline *allylnorhydroxycodeinone*, characterised as the *hydriodide*, decomp. 192°.



(I.)

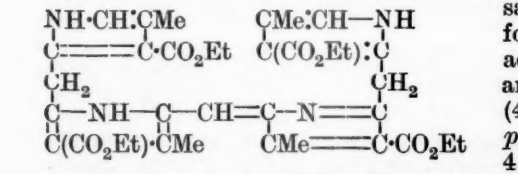
Acetoxydihydronorcodeinone is converted by cyanogen bromide into *cyanoacetoxydihydronorcodeinone*, decomp. 256° after softening. It is converted by sulphuric acid into the oily *hydroxydihydronorcodeinone* (*hydriodide*, decomp. 295°, $[\alpha]_D^{13}$ −114·54° in dilute acetic acid solution; *nitroso* derivative, decomp. 259°). *Allylhydroxydihydronorcodeinone* is a liquid which gives a crystalline *hydrobromide*, decomp. 182°. The pharmacological action of the allyl derivatives is opposite to that of the parent compounds, as is to be expected when the methyl is replaced by the allyl group (cf. von Braun, A., 1917, i, 163).

H. W.

Strychnos Alkaloids. XLIII. Decomposition of the Azide of Dihydrobrucinonic Acid. H. Leuchs and S. Kanao (*Ber.*, 1924, **57**, [*B*], 1318—1320; cf. A., 1923, i, 942).—Ethyl dihydrobrucinonate is converted successively into the corresponding *hydrazide*, decomp. 205° after softening at 185°, and azide. The latter is decomposed by boiling water into azoimide, formalde-

hyde, and an iso*brucinolone hydrate*, $C_{21}H_{24}O_6N_2$, m. p. 295° (decomp.) after darkening at 260°, $[\alpha]_D^{20}$ +89·4° in glacial acetic acid solution (*acetyl* derivative, m. p. 210—212°, $[\alpha]_D^{20}$ +94·8° in glacial acetic acid). The *iso*brucinolone hydrate is not identical with that obtained from *iso*brucinolone and hydrochloric acid (Leuchs and Brewster, A., 1912, i, 210). H. W.

Action of Halogens on Substituted Pyrroles. Synthesis of a Dipyrrylethane and of a Colouring Matter with Four Pyrrole Nuclei in its Molecule. H. FISCHER and H. SCHEYER (*Annalen*, 1924, **439**, 185—195; cf. this vol., i, 80).—Aniline interacts with ethyl 4-methyl-2-bromomethylpyrrole-3 : 5-dicarboxylate (A) to give *ethyl* 4-*methyl*-2-*anilinomethylpyrrole*-3 : 5-*dicarboxylate*, m. p. 125—126°, and with ethyl 3-bromo-4-methyl-2-bromomethylpyrrole-5-carboxylate (B) to give *ethyl* 3-*bromo*-4-*methyl*-2-*anilinomethylpyrrole*-5-*carboxylate*, m. p. 128—129°. (A) also reacts with phenylhydrazine, forming α-(4-*methyl*-3 : 5-*dicarbethoxy*-2-*pyrrylmethyl*)α-*phenylhydrazine*, m. p. 120—121°, the asymmetric structure of which is demonstrated by the fact that with benzaldehyde it affords a *hydrazone*, rhombs, m. p. 116—117°. (B) gives a similar product, namely, α-(3-*bromo*-4-*methyl*-5-*carbethoxy*-2-*pyrrylmethyl*)α-*phenylhydrazine*, m. p. 126°. With hydrazine itself, (A) yields αα-di-(4-*methyl*-3 : 5-*dicarbethoxy*-2-*pyrrylmethyl*)*hydrazine*, m. p. 130—131°, which affords with benzaldehyde a *hydrazone*, m. p. 129—130°, and with ethyl 2 : 4-dimethylpyrrole-3-aldehyde-5-carboxylate also a *hydrazone*, m. p. 162—163° after softening; when the hydrazine is treated with cuprammonium acetate solution, nitrogen is evolved, and s-*di*-(4-*methyl*-3 : 5-*dicarbethoxy*-2-*pyrryl*)*ethane*, needles, m. p. 161°, is produced. The latter suffers hydrolysis to the *dicarboxylic acid* (the *sodium* salt is described) when treated with sodium hydroxide solution, only the two 5-carbethoxy groups being affected; when the sodium salt of this is treated with formic and hydrochloric acids the carboxyl groups are displaced and 5 : 5′-*di*-(4″-*methyl*-3″-*carbethoxy*-β-*pyrrylethyl*-)3 : 3′-*dimethyl*-4 : 4′-*dicarbethoxy*-2 : 2′-*dipyrrylmethene* (annexed formula), m. p. 277° (decomp.), is produced. This is an intensely yellow-coloured substance, closely resembling mesobilirubin in colour.



Ethyl 2 : 4-dimethylpyrrole-5-carboxylate is converted by treatment with bromine (2 mols.) into (B), which was previously obtained (*loc. cit.*) by another method. When 3-acetyl-2 : 4-dimethylpyrrole is treated with iodine 5-*iodo*-3-*acetyl*-2 : 4-*dimethylpyrrole*, m. p. 160° (decomp.), is obtained. The iodine atom here is not very mobile, but when the compound is treated with bromine the same methene is produced as is afforded when the unsubstituted pyrrole is treated with an excess of bromine (*loc. cit.*). *Ethyl* 5-*iodo*-2 : 4-*dimethylpyrrole*-3-*carboxylate*, m. p. 146°, *ethyl* 3-*iodo*-

2 : 4-*dimethylpyrrole*-5-*carboxylate*, m. p. 141°, and *ethyl* 4-*iodo*-2 : 5-*dimethylpyrrole*-3-*carboxylate*, m. p. 136°, are also described. W. A. S.

Synthesis of Phyllopyrrolecarboxylic Acid (Synthesis of the Acid Scission Products of Blood Pigment. II). H. FISCHER and C. NENITZESCU (*Annalen*, 1924, **439**, 172—184; cf. this vol., i, 543).—2 : 4 : 5-Trimethylpyrrole-3-aldehyde reacts with malonic acid in presence of piperidine (the aldehyde forms an *additive* compound with piperidine, m. p. 145°) to yield 2 : 4 : 5-*trimethylpyrrole*-3(β)-*acrylic acid*, a green, not very stable substance, m. p. 203°, which is readily reduced by sodium amalgam to 2 : 4 : 5-trimethylpyrrole-3(β)-propionic acid, m. p. 88° (picrate, m. p. 124°) identical with phyllopyrrolecarboxylic acid obtained from hæmin. When the above aldehyde is condensed with malononitrile, 2 : 4 : 5-*trimethyl*-3-(ωω-*dicyanovinyl*)*pyrrole*, greenish-yellow needles, m. p. 185°, is obtained. This substance resists hydrolysis; by the action of sodium hydroxide, the aldehyde is regenerated, and sulphuric acid causes profound decomposition. By a similar condensation, using cyanoacetic acid, 2 : 4 : 5-*trimethyl*-3-(ω-*cyano*-ω-*carboxyvinyl*)*pyrrole*, green crystals, m. p. 214°, was prepared. This also cannot be hydrolysed, but when heated at its m. p. decomposes, giving 2 : 4 : 5-*trimethyl*-3-(ω-*cyanovinyl*)*pyrrole*, olive-green needles, m. p. 154°, which, when treated with sodium amalgam, undergoes reduction and hydrolysis, giving phyllopyrrolecarboxylic acid, identical with that previously obtained. 2 : 5-Dimethyl-4-carbethoxypyrrole-3-aldehyde also reacts with malonic acid to afford directly 2 : 5-*dimethyl*-4-*carbethoxypyrrole*-3(β)-*acrylic acid*, yellow scales, m. p. 230° (decomp.), which, when reduced with sodium amalgam, yields 2 : 5-*dimethyl*-4-*carbethoxypyrrole*-3(β)-*propionic acid*, m. p. 178°. The latter may also be obtained synthetically by heating with ammonium acetate at 160° the oily ethyl αβ-diacetyladipate formed by interaction of ethyl acetylbromobutyrate and ethyl sodioacetoacetate; the ester obtained is readily hydrolysed by warm potassium hydroxide. When the dimethylcarbethoxypyrrolepropionic acid of either provenance is heated at 220° with potassium methoxide and methyl alcohol, it yields phyllopyrrolecarboxylic acid. W. A. S.

Condensations of Acetyl-*p*-phenylenediamine to Derivatives of Pyrrole and their Hydrolytic Fission. C. BÜLOW and W. DICK (*Ber.*, 1924, **57**, [*B*], 1281—1285).—Ethyl diacetylsuccinate reacts with acetyl-*p*-phenylenediamine in boiling glacial acetic acid solution to yield *ethyl* 1-p-*acetamidophenyl*-2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylate*, m. p. 198—199°, which is hydrolysed by alcoholic potassium hydroxide solution to 1-p-*acetamidophenyl*-2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylic acid*, m. p. 252° (decomp.) [the *potassium* salt and the *hydrochloride* are described]. The acid is transformed at 250—255° into 1-p-*acetamidophenyl*-2 : 5-*dimethylpyrrole*, m. p. 192°, which is also obtained directly from acetonylacetone and acetyl-*p*-phenylenediamine. The ester is very slowly hydrolysed to the corresponding acid by aqueous alkali hydroxides.

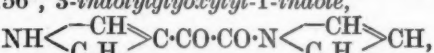
but readily suffers fission of the pyrrole ring into its components under the influence of acids. With hydrazine, it yields the cyclic *hydrazide*, $\begin{matrix}NH\cdot CO\cdot C\cdot CMe\\ NH\cdot CO\cdot C\cdot CMe\end{matrix}\!\!>\!N\cdot C_6H_4\cdot NHAc$, m. p. above 300°. Ethyl diacetylsuccinate and *p*-nitroaniline yield *ethyl* 1-p-*nitrophenyl*-2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylate*, m. p. 94°, which is reduced by zinc dust and hydrochloric acid to *ethyl* 1-p-*aminophenyl*-2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylate*, m. p. 117°. The diazotised ester is coupled with the requisite component to yield *ethyl* 1-p-*aminophenyl*-2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylateazo*-β-*naphthol*, m. p. 166°, *ethyl* 1-p-*aminophenyl*-2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylateazoacetoacetanilide*, m. p. 155°, and the corresponding p-*phenetidide*, m. p. 178°. The latter compounds are converted by phenylhydrazine into the *substance* $\begin{matrix}CO_2Et\cdot C\cdot CMe\\ \|\\ CO_2Et\cdot C\cdot CMe\end{matrix}\!\!>\!N\cdot C_6H_4\cdot N{:}N\cdot C\!<\!\!\begin{matrix}CMe{=}N\\ |\\ C(OH)\cdot NPh\end{matrix}$, m. p. 154—156°. Ethyl 1-*p*-nitrophenyl-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate and ethyl 1-phenyl-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate suffer fission of the pyrrole ring under the influence of mineral acids; this reaction appears therefore to be general. H. W.

Synthesis of 1-Aminocarbazole. H. Lindemann and F. Werther (*Ber.*, 1924, **57**, [*B*], 1316—1318).—7-Nitro-1-phenylbenzotriazole is reduced by stannous chloride and hydrochloric acid to 7-*amino*-1-*phenylbenzotriazole*, $NH_2\cdot C_6H_3\!<\!\!\begin{matrix}N\\ NPh\end{matrix}\!\!>\!N$, m. p. 163° (*acetyl* derivative, m. p. 166°), which, when heated at 300° in paraffin, yields 1-*aminocarbazole*, m. p. 193° (*diacetyl* compound, m. p. 186°). Since the amine is also produced by the action of sodium hyposulphite on an alkaline–alcoholic solution of the nitrocarbazole, m. p. 187°, isolated by Lindemann as by-product of the nitration of nitrosocarbazole (this vol., i, 550), the latter must be 1-nitrocarbazole; the compound described thus in the literature is therefore the 2- or 4-nitro derivative. H. W.

Carbazole Derivatives. I. R. Seka (*Ber.*, 1924, **57**, [*B*], 1527—1530).—Ethyl carbazole-9-acetate is converted by alcoholic ammonia at 120° into *carbazole*-9-*acetamide*, $C_{12}H_8N\cdot CH_2\cdot CO\cdot NH_2$, m. p. 244°, and by hydrazine hydrate at 125° into *carbazole*-9-*acethydrazide*, m. p. 258—258·5° (*benzylidene* derivative, m. p. 267·5°; *hydrochloride*, m. p. above 320°). The hydrazide is converted through the azide into the corresponding *urethane*, $C_{12}H_8N\cdot CH_2\cdot NH\cdot CO_2Et$, m. p. 133·5°. *Diphenyl*-9-*carbazolylmethylcarbinol*, $C_{12}H_8N\cdot CH_2\cdot CPh_2\cdot OH$, m. p. 147°, is prepared by the action of an excess of magnesium phenyl bromide on ethyl carbazole-9-acetate. H. W.

Synthesis in the Indole Group. III. Formation of *N*-Acylindoles. R. Majima and T. Shigematsu (*Ber.*, 1924, **57**, [*B*], 1449—1453).—The addition of ethyl acetate to a solution of magnesium indolyl iodide in ether or anisole leads to the formation of

1-acetylindole; the solvent does not play the same decisive part as in the action of magnesium indolyl iodide and formic ester (Majima and Kotake, A., 1923, i, 150). Magnesium indolyl iodide and ethyl oxalate yield a mixture 1 : 1′-*oxalyldi-indole*, $C_{18}H_{12}O_2N_2$, m. p. 154·5—156°, 3-*indolylglyoxylyl*-1-*indole*,



m. p. 224—225° (which is hydrolysed by potassium hydroxide to indole, and *indolyl*-3-*glyoxylic acid*, decomp. 215° after darkening at 186°), and *ethyl indolyl*-3-*glyoxylate*, m. p. 185—186°. The compound designated 1 : 1-di-indolyl prepared by Oddo and Sanna (A., 1922, i, 371) by the action of oxalyl chloride on magnesium indolyl bromide is 3-indolylglyoxylyl-1-indole.

[With T. Rokkaku.]—Ethyl malonate does not appear to react with magnesium indolyl iodide in the presence of anisole.

[With T. Ikeda.]—Ethyl succinate and magnesium indolyl iodide yield *succinyl*-1 : 1′-*di-indole*, $C_{20}H_{16}O_2N_2$, m. p. 217—218°.

H. W.

Syntheses in the Indole Group. IV. Indolylketonic Acids. R. Majima, T. Shigematsu, and T. Rokkaku (*Ber.*, 1924, **57**, [*B*], 1453—1456).—The action of carbomethoxyformyl chloride on an ethereal solution of magnesium indolyl iodide gives a little 3-indolylglyoxylyl-1-indole (cf. preceding abstract) and, mainly, *methyl* 3-*indolylglyoxylate*, m. p. 220—222° (*phenylhydrazone*, m. p. 133—136°). The *oxime*, m. p. 149—151°, and the *oxime* of the corresponding ethyl ester, m. p. 138—142°, are prepared by means of hydroxylamine hydrochloride and potassium acetate in alcoholic solution. If, however, the ester is warmed with the equivalent quantity of free hydroxylamine, 3-*indolylglyoxylic acid oxime*, decomp. about 151°, is produced. *Ethyl* 3-*indolylacetate*, $C_8H_6N{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$, m. p. 119·5°, prepared from magnesium indolyl iodide and carbethoxyacetyl chloride, is readily transformed by alcoholic potassium hydroxide solution into methyl 3-indolyl ketone. The ester is converted by phenylhydrazine into 1-*phenyl*-3-β-*indolylpyrazolone*, $C_{17}H_{13}ON_3$, m. p. 201—203°, and by hydroxylamine into 3-β-*indolyl*isooxazolone, $C_{11}H_8O_2N_2$, m. p. 188—188·5°.

[With T. Ikeda.]—*Ethyl* β-3-*indolylpropionate*, prepared from magnesium indolyl iodide and β-carbethoxypropionyl chloride, has m. p. 129·5—130·5°; the corresponding *acid*, m. p. 235—236°, is described. The ester is decomposed by molten potassium hydroxide with production of indole-3-carboxylic acid in small amount.

[With I. Miyagawa.]—Cyanogen chloride and magnesium indolyl iodide yield 3-*cyanoindole*, m. p. 178—180·5°. 3-*Cyano*-2-*methylindole*, m. p. 210—212°, is unusually resistant to hydrolysis by alkali hydroxide.

H. W.

New Class of Indigoid Dyes. F. Reindel (*Ber.*, 1924, **57**, [*B*], 1381—1386).—2-Aminopyridine is converted by chloroacetic acid into *pyridylglycine*, $C_7H_8O_2N_2$, m. p. 250° (decomp.), which is transformed by boiling sodium hydroxide solution into the *sodium*

salt of *pyrindoxyl*, $C_5H_3N<^{C(ONa)}_{NH}>CH$ or $NH{:}C_5H_3<^{C(ONa)}_{N}>CH$. The constitution of the salt is thus far established by its ability to give a *monobenzoyl* derivative, m. p. 293° (decomp.) after softening at 275°, which is soluble in alkali hydroxide solution, and an insoluble *dibenzoyl* compound, m. p. 172—173°, when benzoylated according to the Schotten–Baumann reaction, whereas when treated with benzoyl chloride in the presence of pyridine it yields a *benzoyl* derivative, m. p. 130°, which is insoluble in alkali hydroxide. The *barium*, *copper*, *lead*, *cobalt*, and *nickel* salts of pyrindoxyl have been examined; the *hydrochloride*, $C_7H_7ON_2Cl$, m. p. 243° (decomp.) after darkening at 230°, and the *picrate*, decomp. 207—208°, are described. The sodium salt is oxidised by an aqueous solution of potassium ferricyanide to the indigoid *dye*,

$$C_5H_3N<^{CO}_{NH}>C{:}C<^{CO}_{NH}>C_5H_5N$$

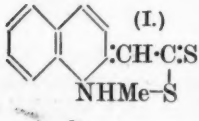
or $C_5H_3(NH)<^{CO}_{N}>C{:}C<^{CO}_{N}>C_5H_3NH$, a red amorphous powder which is readily reduced beyond the indigo-white stage by sodium hyposulphite, but yields a typical vat with zinc dust and sodium hydroxide. On cotton mordanted with tannin and tartar emetic, it gives raspberry-red shades which are fast to light but not to milling. H. W.

Reactions of 2-Methylene-1-alkyl-1 : 2-dihydroquinolines. I. Diazo Coupling of the Methylene Base in Neutral Solution. E. Rosenhauer [with O. Dannhofer] (*Ber.*, 1924, **57**, [*B*], 1291—1294).—2-Methylene-1-methyl-1 : 2-dihydroquinoline dissolved in ether couples with a neutral, aqueous solution of benzenediazonium chloride without loss of the *N*-methyl group (contrast König, A., 1923, i, 862) to form 2-*benzeneazomethylene*-1-*methyl*-1 : 2-*dihydroquinoline hydrochloride*, decomp. 243°, from which the free base, m. p. 140—141°, is obtained; the latter compound is identical with that prepared from 2-bromomethylquinoline methobromide and phenylhydrazine (Rosenhauer, this vol., i, 768). When cautiously oxidised with potassium permanganate, it yields 1-methyl-2-quinolone. Similarly, the methylene base and diazobenzenesulphonic acid give the "internal" p-*sulphonate* of 2-*benzeneazomethylene*-1-*methyl*-1 : 2-*dihydroquinoline*,

$$CH<^{CH—C{:}CH\cdot N{:}N\cdot C_6H_4\cdot SO_2}_{C_6H_4\cdot NHMe\ O}>,$$

decomp. above 300°, which is transformed by sodium hydroxide into the *sodium* salt of 2-*p*-sulphobenzeneazomethylene-1-methyl-1 : 2-dihydroquinoline.

[With A. Schmidt and W. Schleifenbaum.]—2-Methylene-1-methyl-1 : 2-dihydroquinoline dissolved in benzene is converted by a large excess of carbon disulphide into the compound I, decomp. 185°. A similar *substance*, $C_{13}H_{13}NS_2$, decomp. 185°, is derived from 2-methylene-1-ethyl-1 : 2-dihydroquinoline. H. W.



(I.)

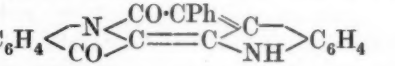
Degradation of Pyridine to Glutacondialdehyde and Reconversion of the Latter into Pyridine. I. P. BAUMGARTEN.—(See i, 1166.)

Cyanine Dyes. VIII. Synthesis of a 2 : 4′-Carbocyanine. Constitution of the Dicyanines. W. H. MILLS and R. C. ODAMS (*J. Chem. Soc.*, 1924, **125**, 1913—1921).—When a mixture of 4-methyl- and 2-methyl-quinoline ethonitrates is heated in pyridine solution with diformylmethylaminodiphenyl disulphide (cf. Mills, Clark, and Aeschlimann, T., 1923, **123**, 2358) six products are formed and may be separated by fractional extraction with and crystallisation from water, benzene, or methyl alcohol, if necessary after conversion into the respective iodides. They are (i) bis-2-methylbenzothiazoline-1 : 1-spiran (Mills and Braunholtz, T., 1923, **123**, 2804); (ii) and (iii) pinacyanole and kryptocyanine (in very small amount); (iv) *2-methyl-1′-ethylthioisocyanine iodide*, m. p. 248—249°, which was prepared also from 4-methylquinoline ethonitrate; (v) *2-methyl-1′-ethylthiopseudocyanine iodide*, m. p. 254—256°, also prepared separately from 2-methylquinoline ethonitrate; and (vi) the main product (the quantity of which showed that condensation between two dissimilar molecules readily takes place), namely, *1 : 1′-diethyl-2 : 4′-carbocyanine iodide*,

m. p. 240—241° (the crystals contain 1 MeOH). This substance is spectrometrically intermediate between pinacyanole and kryptocyanine.

The dicyanine, m. p. 244—252°, from 2 : 4-dimethylquinoline ethiodide (cf. Mikeska, Haller, and Adams, A., 1921, i, 54) was prepared by oxidising the base, in methyl-alcoholic solution, by exposure to the air. The absorption spectrum of this compound is almost identical with that of the above 2 : 4′-carbocyanine; this result and analytical figures show that the compound is *2′ : 4-dimethyl-1 : 1′-diethyl-2 : 4′-carbocyanine iodide*. Presumably it is formed by the linking of 2 mols. of the ethiodide by means of a methenyl group furnished by disruptive oxidation of a portion of the material. W. A. S.

Indigotin Group. IV. New Vat Dye Prepared from Indigotin and Ethyl Phenylacetate. T. POSNER and W. KEMPER (*Ber.*, 1924, **57**, [*B*], 1311—1315).—*Ethyl indigotinphenylacetate* (I), dark violet crystals, m. p. above 320°, is obtained by

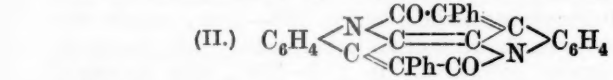


(I.)

protracted ebullition of powdered indigotin with a very large excess of ethyl phenylacetate. A substance, $C_{24}H_{17}O_2N$, m. p. 302°, which has not been investigated further, is obtained as by-product.

It is converted by reduction with sodium hyposulphite in the presence of sodium hydroxide and addition of benzoyl chloride to the solution into *ethyl benzoyldihydroindigotinphenylacetate*, m. p. 235°, and by benzoyl chloride in the presence of boiling pyridine into *ethyl benzoylindigotinphenylacetate*, m. p. 307° (decomp.), thus establishing the presence of the carbonyl and imino groups. Since it is transformed by protracted boiling with ethyl malonate into ethyl anhydrophenylacetylindigotinmalonate, identical with the product obtained by Posner and Pyl (A., 1923, i, 254) from ethyl indigotinmalonate and phenylacetyl chloride, it must contain the group –CO·C:C·NH–. The compound and ethyl indigotinmalonate are of peculiar interest since they can only be derived from the *trans* form of indigotin.

The constitution (II), assigned without stringent proof to Ciba-

(II.) 

red B, is established by its production from ethyl indigotinphenylacetate and ethyl phenylacetate or phenylacetyl chloride. H. W.

Quinazolines. XXXVII. Behaviour of Phthalic Anhydride with the Reactive Methyl Groups of certain Quinazolines. M. T. Bogert and F. P. Nabenhauer (*J. Amer. Chem. Soc.*, 1924, **46**, 1932—1936; cf. A., 1912, i, 214).—An attempt has been made to prepare dyes of the quinoline-yellow type by condensing several quinoxalines with phthalic anhydride and sulphonating the products. 2-Methyl-, 2 : 4-dimethyl-, 2-phenyl-, and 2-phenyl-4-methylquinazolines were prepared (in the main) by methods already described. 4-*Methylquinazoline*, pale yellow prisms, m. p. 36—37° (corr.), b. p. *ca.* 260° (corr.), was prepared by boiling 4-methylquinazoline-2-carbonamide with hydrochloric acid; *picrate*, m. p. 183·5° (corr.). These quinazolines when heated with phthalic anhydride at about 200° showed varying degrees of reactivity; the condensation was more rapid and complete when the methyl group was in the 2-position and the product was insoluble in dilute alkali. The condensation product (phthalone) from the 4-methylquinazolone was soluble in dilute alkali. Since only a small portion of the product from 2 : 4-dimethylquinazoline was soluble in alkali it appears that the 2-methyl had reacted rather than the 4-methyl group. The phthalones in all cases were amorphous and difficult to purify, those from 4-methyl- and 2-phenyl-4-methylquinazolines being incapable of purification. 2-*Methylquinazolinephthalone*, $C_{17}H_{10}O_2N_2$, is a yellowish-brown powder, soluble with a yellow colour in sulphuric acid and organic solvents. Its sulphonation product dyes silk a dull golden-yellow, not very fast to washing. 2 : 4-*Dimethylquinazolinemonophthalone*, $C_{18}H_{12}O_2N_2$, was obtained (impure) as a dark brown powder, insoluble in water and dilute alkali. The ammonium salt of the sulphonation product dyes silk a brown shade. The condensation product (purity, 80%) from 4-methylquinazoline and phthalic anhydride was strikingly different from the above phthalones, being insoluble in ethyl-

benzene and soluble in dilute alkali to a brown solution. Acids precipitated it as a brownish-yellow powder. It is a very strong dye, the dyeings (on silk), however, being less fast to washing than to light. 2-Phenyl-4-methylquinazoline formed only a small amount of condensation product with phthalic anhydride even after 8 hours' heating at 210°; a little of this was soluble in dilute alkali, the insoluble part (still containing unchanged quinazoline) on sulphonation giving a *product* which dyed silk orange. The dyes obtained appear to be decidedly inferior to quinoline-yellow.

A. C.

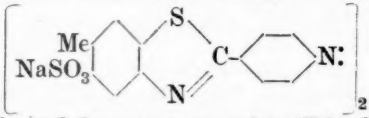
[**Derivatives of *cyclo*Triazobutane.**] R. STOLLÉ (*Ber.*, 1924, 57, [*B*], 1558).—The compound described by Diels and Behncke (this vol., i, 674) as *cyclo*triazomethene-4 : 4-dicarboxylic acid is identified as the hydroxytriazolecarboxylic acid, $\begin{matrix}N{:}C(OH)-\\ |\\ N{:}C(CO_2H)\end{matrix}>NH$, whereas 2 : 4-carbonyl*cyclo*triazomethene is the hydroxytriazole, $\begin{matrix}N{:}C(OH)\\ |\\ N{:}CH-\end{matrix}>NH$.

H. W.

***iso*Oxazoline Oxides. III. Triphenyl*iso*oxazoline Oxide.** E. P. KOHLER and G. R. BARRETT (*J. Amer. Chem. Soc.*, 1924, **46**, 2105—2113).—By the condensation of nitrostilbene with phenylnitromethane in the presence of sodium methoxide (cf. Knoevenagel and Walter, A., 1905, i, 65), 3 : 4 : 5-*triphenyl*iso*oxazoline oxide*, $\begin{matrix}CHPh{\cdot}CHPh\\ |\\ CPh{=\!=}NO\end{matrix}>O$, m. p. 162°, is obtained, in which the only reactive group present is the system C : NO characteristic of *iso*oxazoline oxides (cf. this vol., i, 571, 998). The reaction probably proceeds according to the scheme: $CHPh{:}CPh{\cdot}NO_2 + CH_2Ph{\cdot}NO_2 \rightarrow \begin{matrix}CHPh{\cdot}CHPh{\cdot}NO_2\\ |\\ CHPh{\cdot}NO_2\end{matrix} \rightarrow \begin{matrix}CHPh{\cdot}CHPh\\ |\\ CPh{=\!=}NO\end{matrix}>O$, the dinitro compound having been previously isolated by Hein (A., 1911, i, 717). Triphenyl*iso*oxazole (Meisenheimer, A., 1922, i, 176) is the main by-product of the reaction and its formation is due to "stripping" of the *iso*oxazoline oxide by excess of sodium methoxide since this is rapidly converted into the *iso*oxazole on boiling with concentrated aqueous-alcoholic sodium hydroxide. Dilute bases have little action (cf. *loc. cit.*), and the mechanism of the "stripping" is not clear, as no evidence could be obtained of the intermediate formation of a ketolic oxime, HO·N:CPh·CPh:CPh·OH. The oxide is not "stripped" by acetic acid, but loses water when heated alone, yielding *iso*oxazole and benzonitrile. Nitrous acid in acetic acid and permanganate in acetone do not attack the oxide, but with chromic acid in acetic acid phenyldibenzoylmethane (Meisenheimer, *loc. cit.*) was obtained. Bromine in acetic acid gave, besides *iso*oxazole, a small amount of a nitrogen-free *substance*, m. p. 125°. In other reactions also, the new *iso*oxazoline oxide shows marked differences from the oxides previously obtained, which contained acyl groups. With phosphorus pentachloride, it behaves like diphenylfuroxan, oxygen being removed, yielding 3 : 4 : 5-*triphenyl*-

*iso*oxazoline, m. p. 136—137°, which does not react with magnesium ethyl bromide, and is oxidised to triphenyl*iso*oxazole by chromic acid. Reduction with zinc and acetic acid converts the oxide into a stable *substance*, m. p. 188°, which yields an *acetyl* derivative, m. p. 100—110° (decomp.), a *benzoyl* derivative, m. p. 130°, and a *copper* derivative with cupric acetate; the structure 2-*hydroxy*-3 : 4 : 5-*triphenyl*iso*oxazoline* is accordingly assigned to it (cf. Posner, A., 1907, i, 55), the acidic properties being attributed to the NOH group. Concentrated sulphuric acid transforms this reduction product into (1) a 3 : 4 : 5-triphenyl*iso*oxazoline, m. p. 208°, isomeric with the product obtained by the action of phosphorus pentachloride on the *iso*oxazoline oxide ; (2) triphenyl*iso*oxazole, and (3) 3 : 4 : 5-*triphenyl*iso*oxazolidine*, m. p. 96°, which reacts with magnesium ethyl bromide, yields a nitroso compound, and is identical with the main product of the action of sulphuric acid on the oxide. Only small amounts of the *iso*oxazole are formed, and the relative amounts of this and the *iso*oxazolidine do not accord with a reciprocal oxidation–reduction reaction. Triphenyl-*iso*oxazoline oxide reacts with a large excess of magnesium ethyl bromide, giving, in 50% yield, the above 2-hydroxy-3 : 4 : 5-triphenyl*iso*oxazoline. R. B.

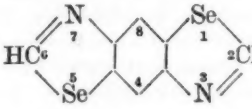
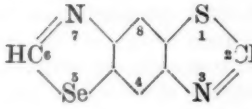
Constitution of Columbia-yellow (Chloramine-yellow). M. T. Bogert and F. H. Bergeim (*Proc. Nat. Acad. Sci.*, 1924, **10**, 318—322).—Columbia-yellow is assigned the formula



The position of the sulphonate groups is still in doubt. Specimens of the dye purified through the free sulphonic acid and its cerium salt give analyses and molecular weights agreeing with this formula. The dye was synthesised by reducing 2-*p*-nitrophenyl-6-methylbenzthiazole to the azo compound by means of zinc and alkali, and subsequently sulphonating; the product was physically, chemically, and tinctorially identical with Columbia-yellow. The lower homologue of this dye was prepared by oxidising sodium 2-*p*-aminophenylbenzthiazolesulphonate with sodium hypochlorite and proved to be a substantive dye of a lighter shade but very similar properties. Hence the methyl groups are not essential for the production of this type of dye, and in the usual method of preparation of Columbia-yellow by the action of sodium hypochlorite on sodium dehydrothio-*p*-toluidinesulphonate it is the amino group which is oxidised, and not, as has been suggested, the methyl group, giving rise to a stilbene derivative. The oxidation of the amino group may produce an azo compound, a quinone, a quinoneimine, a chloroimine, or a chloroamine. Since the purified dye contains no chlorine, the two latter are excluded. The resistance to oxidation and reduction exhibited by Columbia-yellow is an argument against quinone structure and further evidence in this direction was supplied by the observation that 2-*p*-hydroxyphenyl-

6-methylbenzthiazolesulphonic acid (prepared by diazotisation from dehydrothio-*p*-toluidinesulphonic acid) did not give a dye or a colour reaction when oxidised by sodium hypochlorite. S. S.

Selenium Organic Compounds. IV. Synthesis of Benzobis-selenazoles and Selenazolobenzothiazoles; New Heterocyclic Systems. M. T. Bogert and H. H. Hopkins (*J. Amer. Chem. Soc.*, 1924, **46**, 1912—1917).—The new heterocyclic types: (I) benzobis-selenazoles and (II) selenazolobenzthiazoles have been prepared by fusion of benzylideneaminobenzoselenazoles with selenium and with sulphur. 2 : 6-*Diphenyl*-p-β-*benzobis-selenazole*

(I.)  (II.) 

lemon-yellow needles, m. p. 217°, was obtained in 17% of the theoretical yield by boiling 6-benzylideneamino-2-phenylbenzoselenazole with selenium. As proof of its structure it was also synthesised by fusing dibenzylidene-*p*-phenylenediamine with selenium. A mixture of the two products had the same m. p. It forms an unstable *acetyl chloride additive* product; a *nitro* derivative, m. p. 296·1—297·1°; a *dinitro* derivative, m. p. 332·4—333·4°. The nitro compound on reduction with tin and hydrochloric acid gives *amino*-2 : 6-*diphenyl*-p-β-*benzobis-selenazole* (yield 30%), orange needles, m. p. 279·4—281°; it formed a *benzylidene* derivative, m. p. 233·5—235·5°, when heated in boiling *n*-butyl-alcoholic solution with benzaldehyde. 2 : 6-*Diphenyl*-p-β-*selenazolobenzthiazole*, m. p. 220·4—221·5°, b. p. 345—350°/11 mm., was obtained as lustrous yellow needles from the mass formed on fusing 6-benzylideneamino-2-phenylbenzoselenazole with sulphur at 250—260°; the *tetrabromide* decomposed at 238—243°, and slowly on keeping; an *acetyl chloride additive* product melted at 224—225° with evolution of acetyl chloride; the *dinitro* derivative had m. p. 295—297°, and probably contained some mononitro derivative. The selenazolothiazole did not combine with methyl iodide in a sealed tube at 100°. One of the experiments for the preparation of the selenazolothiazole resulted in a 25% yield of a new *base*, $C_{27}H_{18}N_2S_2Se$, long, straw-coloured needles, m. p. 5° higher than the selenazole and quite distinct from it. The base gave a *dinitro* derivative, m. p. 283°, which on reduction yielded the *compound* $C_{27}H_{20}N_4SSe$, brownish-yellow needles, m. p. 305° (decomp., with evolution of hydrogen sulphide). The character of the base was not ascertained, since, although numerous attempts were made, it could not be formed again. 6-*Furfurylideneamino*-2-*phenylbenzoselenazole*,

$$C_{18}H_{12}ON_2Se,$$

yellow needles, m. p. 147·5°, was prepared by heating 6-amino-2-phenylbenzoselenazole with excess of furfuraldehyde. Attempts to combine it with selenium were unsuccessful, as it charred below the m. p. of selenium. No pure product was obtained on heating the furfurylideneamino compound with sulphur. A. C.

Naphthalene and its Derivatives. N. Vorosecov (*Bull. Soc. chim.*, 1924, [iv], **35**, 996—1021).—The dissociation in aqueous solution of the *sodium hydrogen sulphite* compounds of benzeneazo-α-naphthol, yellow needles, benzeneazo-β-naphthol ($+2H_2O$), brilliant golden-yellow spangles, obtained by the action of sodium hydrogen sulphite on the pure azo compound, and of 5-hydroxynaphthaleneazophenol, obtained by coupling phenol with the diazotised sodium hydrogen sulphite compound of 1 : 5-aminonaphthol, has been examined. In all cases, dissociation into azo compound and sulphite increases with the dilution and with the alkalinity of the solution, a very small increase in the number of hydroxyl ions producing a marked increase in the dissociation, whilst in acid solution the dissociation is very slightly retarded, and decreases slightly with increasing concentration of the acid. These results show that the three sulphite compounds have a similar structure and are to be regarded essentially as additive compounds, in opposition to Bucherer's views (A., 1904, i, 309). The formation of such additive compounds will depend on the nature of the conjugated system and the positions of the substituents in the ring, the systems –C(OH):C·C:CX– and –C(OH):CX– favouring the reaction, whilst the systems –C(OH):CH·CX:CH– and –CH:C(OH)·CH:CX–, existing in the 3-substituted α-naphthols and 4-substituted β-naphthols, do not favour addition, and consequently the Bucherer reaction does not take place (cf. Meyer and Lenhardt, A., 1913, i, 704, 723). The different behaviour of the two amino groups in 1 : 5- and 1 : 8-naphthylenediamine with sodium hydrogen sulphite finds an explanation in the different character of the two benzene rings in the naphthalene molecule; one ring behaves as a conjugated olefinic system and yields the additive compound, leading to the naphthol, whilst the other behaves as an aromatic ring system and yields no additive product. The alkylation of the naphthols is similarly explained as due to the formation of an intermediate additive compound, and the conversion of naphthols into naphthylamines and the reverse reaction in the absence of sulphites are given a similar interpretation. The naphthols and naphthylamines from this point of view are intermediate in reactivity between the reactive conjugated open-chain compounds, such as ethyl acetoacetate or β-aminocrotonate, and the typical aromatic phenols and amines of the benzene series. The readiness with which phenols, such as nitrosophenol, phloroglucinol, and nitroso-β-naphthol, which are capable of tautomeric change, are converted into amines also supports the theory (cf. Fuchs and Stix, A., 1922, i, 451; Friedländer, A., 1921, i, 443).

R. B.

Optically Active Dyes. II. Adsorption, Absorption Spectra, and Rotation. W. R. Brode and R. Adams (*J. Amer. Chem. Soc.*, 1924, **46**, 2032—2043).—In continuance of their projected investigation of the question whether the absorption of dyes by animal or vegetable fibres is a physical or chemical process, using the previously described β-naphthol derivatives of *d*-, *l*-, and *dl*-*p*-diazobenzamidophenylacetic acid (Ingersoll and Adams, A.,

1923, i, 200), the authors have established that the adsorption of the two optically active forms of the dye by inactive adsorbing agents, such as charcoal and ball-clay, is identical, but is rather less than that of the racemic form, which also exists more in a colloidal state than do the *d*- and *l*-compounds. The absorption spectra of the active forms of the dye show bands of the same frequency, and variation of the hydrogen-ion concentration of the solutions changes the intensity, but not the wave-length of the bands (cf. A., 1922, ii, 602). Within the range of hydrogen-ion concentration change caused by the addition of common adsorbing agents, the change of colour of the active forms of the dye and the possible difference in the intensity is negligible as far as colorimetric determinations are concerned. Beer's law is valid for the dilute solutions used in these experiments and as far as studied the rotation of the two active dyes is normal. On long standing with sodium hydroxide, racemisation of the active forms takes place, and from saturated solutions of the active forms, the less soluble *dl*-form separates. In view of these facts, it is concluded that any difference in the adsorption of the *d*- and *l*-forms of the dye in the dyeing experiments may be taken as evidence of chemical reaction in the dyeing process. R. B.

Influence of Sulphur on the Colour of Azo Dyes. D. G. Foster and E. E. Reid (*J. Amer. Chem. Soc.*, 1924, **46**, 1936—1948).—By methods very similar to those employed for the para-analogues (cf. this vol., i, 95), a number of *o*-aminophenyl alkyl sulphides have been made by condensing sodium *o*-nitrothiophenoxide with alkyl halides and reducing the nitro compound with iron and acetic acid. Diamines of the type $(NH_2 \cdot C_6H_4 \cdot S \cdot)_2R$, with sulphur have been made in the same way from alkylene dihalides. In many cases, the *o*-nitrophenyl alkyl sulphides were not isolated but reduced at once to the corresponding amino compounds, but the following were prepared in the pure state: *ethyl*, b. p. 149—150°/15 mm., *propyl*, b. p. 172—174°/7 mm., *allyl*, m. p. 54°, the respective yields being 46, 64, 32% of the theoretical. The *allyl sulphide*, m. p. 38—39°, and the cyclo*hexyl sulphide*, m. p. 56—57° of the para-analogue were also prepared. All the amines of this series are oils which decompose below their boiling points, even under diminished pressure. They were isolated as hydrochlorides as white, crystalline solids, $R \cdot S \cdot C_6H_4 \cdot NH_2,HCl$ (the figures represent the % of the theoretical yield on the alkyl halide). *Methyl* (74), *ethyl* (73), *propyl* (54), iso*propyl* (99), *butyl* (55), iso*butyl* (72), iso*amyl* (71), cyclo*hexyl* (32), *allyl* (75). *Allyl*- and cyclo*hexyl*-p-*aminophenyl sulphides* were isolated as sulphates in 45 and 93% of the theoretical yields, respectively. The following o : o'-*dinitrodiphenyl disulphides* are described: $(C_6H_4 \cdot NO_2)_2S_2CH_2$, m. p. 170° from methylene iodide; $(C_6H_4 \cdot NO_2)_2S_2(CH_2)_2$, m. p. 205°, from ethylene dibromide; $(C_6H_4 \cdot NO_2)_2S_2(CH_2)_3$, m. p. 140°, from trimethylene bromide, and $NO_2 \cdot C_6H_4 \cdot S \cdot C_2H_4 \cdot S \cdot C_2H_4 \cdot S \cdot C_6H_4 \cdot NO_2$ (a trisulphide), m. p. 107—108°, from *pp*-dichlorodiethyl sulphide and sodium *o*-nitrothiophenoxide. The last four substances are

very sparingly soluble yellow solids. On reduction the corresponding diamines were obtained as brown oils; their hydrochlorides (which hydrolyse very rapidly) could not be obtained crystalline, but were precipitated from alcohol by means of ether:

$(C_6H_4\cdot NH_2)_2S_2CH_2,2HCl$, $(C_6H_4\cdot NH_2)_2S_2(CH_2)_2,2HCl$, $(C_6H_4\cdot NH_2)_2S_2(CH_2)_3,2HCl$ and $(C_6H_4\cdot NH_2\cdot S\cdot C_2H_4)_2S,2HCl$

were obtained in 91, 21, 89, and 90% of their respective theoretical yields. For the purpose of demonstrating the effect of the sulphone group (on the character of the dyes described below), as compared with the sulphur atom alone, the following *o*-nitrophenylsulphones (white, crystalline solids) were prepared by the method described for the para compounds: $NO_2\cdot C_6H_4\cdot SO_2Me$, m. p. 104—105°; $NO_2\cdot C_6H_4\cdot SO_2Pr$, m. p. 50°; $(NO_2\cdot C_6H_4\cdot SO_2\cdot CH_2)_2CH_2$, 156—157° in 65, 86, and 72% of the respective theoretical yields. The *o*-nitrophenylmethyl and propyl sulphones gave the corresponding *amines*, $NH_2\cdot C_6H_4\cdot SO_2Me$, an oil, and $NH_2\cdot C_6H_4\cdot SO_2Pr$, m. p. 50°, in 69 and 53% of the theoretical yields, but the trimethylene nitrosulphone was reduced to the amine of the disulphide,

$$NH_2\cdot C_6H_4S(CH_2)_3\cdot S\cdot C_6H_4\cdot NH_2.$$

One of the sulphones of the para series behaved similarly. Dyes were made from all the above *o*-nitrophenyl alkyl sulphides and disulphides and sulphones by diazotisation and coupling with R-salt; only the free mercaptan, $NH_2\cdot C_6H_4\cdot SH$, failed to couple and give a dye. They dyed wool red, orange, and yellow shades. A comparison with similar sulphur-free dyes from known intermediates gave: –Me *deep salmon*, –OMe *carmine*, –SMe *yellowish-red*, $-SO_2Me$ *orange*, *i.e.*, in the dyes containing sulphur the characteristic wave-length moves from the red towards the yellow whilst the methoxyl group appears more strongly bathochromic than the alkyl sulphide. In general, the bathochromic effect is much less marked than with sulphur in the para position. In the simple alkyl sulphides, increase in the molecular weight of the alkyl group attached to the sulphur produces a general hypsochromic effect, showing a periodicity in colour similar to that shown in certain physical constants of aliphatic homologous series. The dyes formed from the *o*-diamine bases are markedly different from the benzidine dyes both as to colour and in the fact that none of the ortho dyes are substantive. A hypsochromic effect is shown with reference to the sulphur-free dye when the two sulphur atoms are separated by only one carbon atom. Increasing separation and the introduction of a third atom of sulphur show a bathochromic influence with respect to the other sulphur dyes of the series. The colour relation to the sulphur-free dye is difficult to place. A. C.

Formation of Dyes on Animal Fibres by Reaction of the Material Itself. J. GROOT (*Chem. Weekblad*, 1924, **21**, 450—455).—Wool, silk, hair, and other animal fibres react with nitrous acid, acquiring an intense yellow colour, which may be discharged by sunlight, heating, or the action of alkalis. The action is slow, requiring about 20 hours in the cold. After treatment and thorough washing, the fabric on treatment with phenols or amines acquires

distinctive colours. The coupling takes place in faintly acid or alkaline solutions, and the colours are fast to light and washing, but not to acids and alkalis. Subsequent treatment with metallic salts or with dichromate modifies the colours obtained; the mechanical strength of the fabrics is not adversely affected. The reaction appears to be a true diazotisation of the amino groups of the fibre proteins. S. I. L.

Condensation Products of Aminoarsanilic Acid (3 : 4-Diaminophenylarsinic acid). W. L. Lewis, P. L. Cramer, and R. S. Bly (*J. Amer. Chem. Soc.*, 1924, **46**, 2058—2065).—With a view to study their therapeutic properties a number of arsinated quinoxalines have been prepared by the condensation of 3 : 4-diaminophenylarsinic acid with *o*-diketones. The condensation of 3 : 4-diaminodiphenylarsinic acid with cyanogen and with ω-bromoacetophenone yields dihydroquinoxalines, but with monocarbonyl compounds, such as benzaldehyde, a series of arsenated Schiff's bases is obtained: $H_2O_3As{\cdot}C_6H_3(NH_2)_2+2PhCHO=2H_2O+AsH_2O_3{\cdot}C_6H_3(N{:}CHPh)_2$. The behaviour of ethyl acetoacetate is exceptional and a condensation product of 1 mol. of amino-acid with 1 mol. of acetone is obtained: $AsH_2O_3{\cdot}C_6H_3(NH_2)_2+Ac{\cdot}CH_2CO_2Et \longrightarrow EtOH+CO_2+AsH_2O_3{\cdot}C_6H_3(NH)(N{:}CMe_2)$, a product which cannot be obtained directly from acetone.

3 : 4-Diaminodiphenylarsinic acid, obtained by Bertheim's method (A., 1911, i, 1055), using Jacobs and Heidelberger's method of reduction with ferrous hydroxide (A., 1919, i, 50), with diacetyl in absolute alcohol, yields 2 : 3-*dimethylquinoxaline*-6-*arsinic acid*, lustrous, pink flakes, m. p. 212—215° (decomp.). Similarly, in boiling methyl-alcoholic solution benzil gives 2 : 3-*diphenylquinoxaline*-6-*arsinic acid*, a white or slightly yellow substance (yield 64%), which on treatment with 50% hydrobromic acid in boiling acetic acid yields 2 : 3-*diphenylquinoxaline*-6-*arsenious bromide*,

$$Br_2AsC_6H_3<\begin{matrix}N{:}CPh\\ |\\ N{:}CPh\end{matrix}>,$$

lustrous, yellow plates, m. p. 232°; the corresponding *dihydroxide* is white and the *chloride* has m. p. 185—187°; the *iodide* is described. The *dihydroxide* condenses with chloroacetic acid in alkaline aqueous-alcoholic solution (cf. Adams and Quick, A., 1922, i, 600), yielding 2 : 3-*diphenylquinoxaline*-6-*arsinoacetic acid*,

$$CO_2H{\cdot}CH_2{\cdot}AsO_2H{\cdot}C_{20}H_{13}N_2,$$

m. p. 122—125° (decomp.). 3 : 4-Diaminodiphenylarsinic acid and dinitrobenzil (Barnett and Kay, A., 1922, i, 844) in methyl alcohol give (yield 75%) 2 : 3-*di*-m-*nitrophenylquinoxaline*-6-*arsinic acid*, m. p. above 230° and giving a deep red solution in alkali. Similarly with anisil, prepared from oxalyl chloride and anisole by Staudinger's method (A., 1912, i, 567), is obtained, in 61% yield, 2 : 3-*di*-p-*methoxyphenylquinoxaline*-6-*arsinic acid*, light yellow needles, and with furil, 2 : 3-*difurylquinoxaline*-6-*arsinic acid*, m. p. above 250°. In glacial acetic acid are obtained similarly, from phenetil (*pp'*-diethoxybenzil), m. p. 150—151° (cf. Vorländer, A., 1911, i, 865), prepared by Staudinger's method, 2 : 3-*di*-p-*ethoxyphenylquinoxaline*-

6-*arsinic acid*, light yellow (yield 84%); from piperil (3 : 4-dimethylenedioxy-3′ : 4′-methylenedioxybenzil, 2 : 3-*di*-3 : 4-*methylenedioxyphenylquinoxaline*-6-*arsinic acid*, yellow crystals (yield 92%); and from tetramethyldiaminobenzil, 2 : 3-*di*-p-*dimethylaminophenylquinoxaline*-6-*arsinic acid*, yellow powder, m. p. above 260° (yield 45%). 3 : 4-Diaminophenylarsinic acid and cyanogen combine in methyl alcohol, giving 2 : 3-*di-imino*-1 : 4-*dihydroquinoxaline*-6-*arsinic acid*, $H_2O_3As\cdot C_6H_3<\begin{matrix}NH\cdot C:NH\\ |\\ NH\cdot C:NH\end{matrix}$, orange powder, m. p. 200—205° (decomp.), and ω-bromoacetophenone similarly yields 3(?)-*phenyl*-1 : 2-*dihydroquinoxaline*-6-*arsinic acid*,

$$H_2O_3As\cdot C_6H_3<\begin{matrix}NH\cdot CH_2\\ |\\ N=CPh\end{matrix},$$

orange crystals, m. p. above 250°.

[With E. A. Larsen.]—With ethyl acetoacetate in boiling methyl alcohol, 3 : 4-diaminodiphenylarsinic acid gives in 88% yield 4-*dimethylmethyleneamino*-3-*aminophenylarsinic acid*, m. p. above 260°. Similarly, aldol gives (yield 26%) 3 : 4-*di*-γ-*hydroxybutyleneaminophenylarsinic acid*, $H_2AsO_3\cdot C_6H_3[N:CH\cdot CH_2\cdot CHMe(OH)]$, m. p. below 260°; with crotonaldehyde is obtained 3 : 4-*dicrotonylideneaminophenylarsinic acid*, $H_2AsO_3\cdot C_6H_3(N:CH\cdot CH:CHMe)_2$, m. p. above 260°; with benzaldehyde, 3 : 4-*dibenzylideneaminophenylarsinic acid*, yellow, m. p. above 250° (yield 28%); with *o*-methoxybenzaldehyde, 4-*o*-*methoxybenzylideneamino*-3-*aminophenylarsinic acid*, m. p. above 250°; with anisaldehyde, 4-*p*-*methoxybenzylideneamino*-3-*aminophenylarsinic acid*, yellow powder, and with piperonal, 4-*piperonylideneamino*-3-*aminophenylarsinic acid*,

$$H_2AsO_3\cdot C_6H_3(NH_2)(N:CH\cdot C_6H_3\cdot O_2CH_2).$$

With the object of obtaining a substance with pharmacological properties analogous to tryparsamide (Jacobs and Heidelberger, A., 1920, i, 108), 3 : 4-diaminodiphenylarsinic acid in sodium hydroxide was condensed with chloroacetamide, giving (yield 58%) 4(?)-*acetamidoamino*-3-*aminophenylarsinic acid*,

$$H_2AsO_3\cdot C_6H_3(NH_2)(NH\cdot CH_2\cdot CO\cdot NH_2),$$

decomp. 220—232°. R. B.

Arsenobenzene Derivatives. A. Contardi and U. Cazzani (*Atti I. Congr. naz. Chim. pur. appl.*, 1923, 329—338; from *Chem. Zentr.*, 1924, i, 2512).—3 : 3′-Diamino-4 : 4′-dihydroxyarsenobenzene (salvarsan) forms with dilute (2·5—20%) solutions of dextrose a *monoglucoside*, $[:As\cdot C_6H_3(NH_2,HCl)\cdot O\cdot C_6H_{11}O_5]_2,2H_2O$, a yellow powder having $[\alpha]_D^{20}$ −137·1°. It forms a *picrate* with 2 mols. of picric acid. The *diglucoside*,

$$OH\cdot C_6H_3(NH_2)\cdot As:As\cdot C_6H_3(OH)\cdot NH\cdot C_6H_{11}O_5,$$

formed with more concentrated solutions of dextrose is similar to the monoglucoside. Similar glucosides are given by galactose, α-arabinose, and rhamnose. Neosalvarsan, "neojacol," and "sulpharsenol" also yield glucosides with dextrose. Ethylene glycol yields with salvarsan a *compound*

$$OH\cdot C_6H_3(NH_2)\cdot As:As\cdot C_6H_3\cdot NH\cdot CH_2\cdot CH_2\cdot OH.$$

G. W. R.

New Organic Arsenic Compounds. O. MARGULIES (Brit. Pat. 220668).—When mono- or poly-amino derivatives of aromatic aldehydes or ketones, or of mixed aliphatic-aromatic ketones, are diazotised and treated with an arsenite in aqueous solution, the carbonyl group is not attacked and arsinic acids of therapeutic value are obtained. Preparations, by this method, of the following compounds are described: *Nitroxyacetophenonearsinic acid*, m. p. about 200°; *acetophenone*-p-*arsinic acid*, m. p. about 176°; *benzophenone*-p-*arsinic acid*, m. p. 195—197°; *benzophenone*-4 : 4′-*diarsinic acid*, m. p. 236°; p-*aldehydophenylarsinic acid*; 3-*hydroxybenzophenone*-4′-*arsinic acid*, m. p. 180°; 4-*acetamidobenzophenone*-3′-*arsinic acid*, m. p. 253°; ω-*phthalimidoacetophenone*-p-*arsinic acid*, m. p. not below 270°; *phenyl*-p-*arsinic acid benzyl ketone*, m. p. 160° (decomp.); *propiophenone*-p-*arsinic acid*, m. p. not below 275°; and *nitro*-p-*aldehydophenylarsinic acid*, decomp. 130°. [Cf. *B.*, Nov. 28th.] F. G. W.

Preparation of o-Nitrodiphenylarsinic Acid. E. SAKELLARIOS (*Ber.*, 1924, **57**, [*B*], 1514—1515).—*o*-Nitrodiphenylarsinic acid is prepared in 87% yield by the addition of a solution of phenylarsenious oxide in sodium hydroxide and sodium acetate to a diazotised solution of *o*-nitroaniline in hydrochloric acid. H. W.

Preparation and Properties of Diphenyl-4 : 4′-diarsinic Acid. [MISS] A. E. HILL (*J. Amer. Chem. Soc.*, 1924, **46**, 1855—1857).—It has been sought to extend the inhibiting effect on the growth of certain bacilli possessed by organic substances having the so-called benzidine configuration (cf. Lewis, *J. Exp. Med.*, 25, 441) by combining it with other substances which are known to be therapeutically active in other directions. *Diphneyl*-4 : 4′-*diarsinic acid* was prepared by the Bart reaction from tetrazotised benzidine (cf. A., 1913, i, 115, 415). The acid forms white crystals, is characterised by extreme inertness and stability, and is insoluble in the common organic solvents; it dissolves in boiling water to the extent of 0·1%, in hot sulphuric acid and in hot glycerol without change, and is not attacked by bromine or iodine. It is not sulphonated by fuming sulphuric acid. It is tetrabasic and differs from the diphenylarsinic-*o*-arsinic acid of Kalb (cf. A., 1921, i, 375). The *tetrasodium* salt, white, columnar crystals, contained $14H_2O$ (cf. following abstract). A. C.

Diarsonodiphenyl [Diphenyl-4 : 4′-diarsinic acid] and Derivatives. W. W. BAUER and R. ADAMS (*J. Amer. Chem. Soc.*, 1924, **46**, 1925—1931).—Various arsenic derivatives of diphenyl of possible therapeutic value have been prepared. Tetrazotised benzidine and alkaline sodium arsenite afforded diphenyl-4 : 4′-diarsinic acid, not melting below 300°, being practically insoluble in ordinary solvents. A brown by-product, not obtained pure, appears to be 4-hydroxydiphenyl-4′-arsinic acid. Attempts to nitrate the diarsinic acid were unsuccessful, complex oxidation resulting. It was, however, found possible to prepare, from

3 : 3′-dinitrobenzidine, 3 : 5′-*dinitrodiphenyl*-4 : 4′-*diarsinic acid* (yield, 65%), a light yellow, insoluble solid. The amino groups in 2 : 2′-dinitrobenzidine could not be readily displaced by arsinic acid groups. 3 : 5-*Diaminodiphenyl*-4 : 4′-*diarsinic acid* was obtained as a yellowish-white powder (79% yield), by the reduction of the corresponding dinitro compound with alkaline ferrous hydroxide. It showed all the properties of aminoarsinic acids of the benzene series, and gave a white *diacetyl* derivative. Tetrazotised 3 : 5′-diaminodiphenyl-4 : 4′-diarsinic acid couples with 2 mols. of H-acid to form a dye, $C_{32}H_{26}O_{20}N_6S_4As_2$, of the trypan-blue type, a bronze-coloured solid soluble in water to a bluish-red solution. *o*-Tolidine afforded similar compounds: 3 : 5′-*dimethyldiphenyl*-4 : 4′-*diarsinic acid* (yield, 44%) is a white powder, insoluble in water and organic solvents, and does not melt below 310°. On oxidation with alkaline permanganate, it gives 3 : 5′-*dicarboxydiphenyl*-4 : 4′-*diarsinic acid*, fine, white crystals insoluble in water. Compounds containing an arsinic acid radical attached to one ring and a hydroxyl or amino group attached to the other were also prepared. The best method consisted in forming the tetrazo compound, coupling one diazonium group with a component which could be reduced to an amino group, and then replacing the second diazonium group by an arsinic acid radical. 4-*Aminodiphenyl*-4′-*arsinic acid* was prepared in this manner, using H-acid for the coupling. After the introduction of the arsinic acid group, the product is reduced with sodium hyposulphite and the resulting 4 : 4′-di-*p*-aminodiphenylarsenobenzene, $(NH_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}As{:})_2$, separated from the amino-H-acid, making use of its insolubility in alkali. The arseno compound, when oxidised with alkaline hydrogen peroxide, gives the aminoarsinic acid (*acetyl* derivative, a white solid). Pharmacological tests showed the acetyl derivative to have about the same toxicity as arsanilic acid, whilst 3 : 5′-diaminodiphenyl-4 : 4′-diarsinic acid is much less toxic (cf. preceding abstract).

A. C.

Complex Organic Compounds of Mercury. W. Schoeller (D.R.-P. 387850; U.S. Pat. 1457675; from *Chem. Zentr.*, 1924, i, 2397—2398).—Complex organic compounds of mercury are prepared having the general formulæ XHg·R·R·HgX and

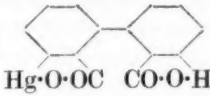
$$XHg{\cdot}R{\cdot}B{\cdot}R{\cdot}HgX,$$

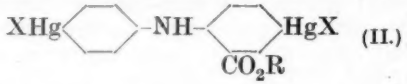
respectively, where X denotes a simple group such as Cl, SO_4, or OAc and R and B complex organic groups. Such compounds when treated with ammonium sulphide yield cyclic compounds in which the two mercury atoms are connected by a sulphur atom. Diethyl diallylmalonate gives with mercuric acetate a complex *ester*, which yields on treatment with sodium chloride solution and subsequent hydrolysis a *dicarboxylic acid*,

$$(CO_2H)_2{\cdot}C(CH_2{\cdot}CH[HgCl]{\cdot}CH_2{\cdot}OEt)_2.$$

Complex mercury compounds may also be prepared with diallylbarbituric acid and ethyl diallylacetate, respectively. Diethyl *o*-phenylenediacrylate yields with mercuric acetate a complex mercury *compound*, $C_6H_4(CH[OMe]{\cdot}CHgX{\cdot}CO_2Et)_2$. From diphenic

acid and mercuric acetate *bismercuroxydiphenic anhydride* (I) is

(I.) 

(II.) 

obtained. Similarly, ethyl diphenylamine-2-carboxylate yields the complex type (II). G. W. R.

Ring Formation in Additive Compounds. I. Cyclic Molecular Compounds of the Stannic Halides. W. HIEBER (*Annalen*, 1924, **439**, 97—131; cf. Pfeiffer and others, A., 1917, i, 205, etc.; and "Organische Molekülverbindungen," Stuttgart, 1922).—Molecular-weight determinations (by the cryoscopic method in ethylene bromide solution) show that the compounds,

$$(R\cdot CO_2R')_2,SnCl_4,$$

formed by union of various esters with stannic chloride, are dissociated to varying degrees in solution. Those from the esters of benzoic acid are almost completely dissociated, but the ethyl β-phenylpropionate compound is more stable and that from ethyl cinnamate is hardly split up at all. Stability here runs parallel with melting-point and resistance to attack by moisture. The extent to which dissociation takes place depends in each case on the concentration and also on the nature of the solvent; nitrobenzene is more active than ethylene bromide, although even in the former the benzaldehyde–stannic chloride additive compound is stable.

The above determinations were made as a preliminary to an investigation of the molecular structure of the compounds obtained from stannic halides and the esters of dibasic acids and related compounds. These compounds are formed by union of equimolecular proportions of the components, and Pfeiffer's formula (*loc. cit.*), which is unsatisfactory for stereochemical reasons, is shown to be incorrect. Molecular-weight determinations indicate that in every case the compounds have the formula

$$[(CH_2)_n(CO_2R)_2,SnCl_4]_2;$$

they are dissociated to varying degrees in solution, but the observed molecular weight is always greater than that required by the simple formula.

The following new compounds are described (a number of others, already described by Pfeiffer and others, were also investigated); all were prepared in a special apparatus designed to secure anhydrous conditions. The *additive* compounds of stannic chloride with various esters have melting points as follows: methyl oxalate, 86°; methyl malonate (needles), 154°; methyl adipate (needles), 132°; methyl pimelate, 116°; methyl suberate (prisms or needles), 110°; methyl azelaate and methyl sebacate, 95° and 90°, respectively. The existence of these compounds by itself, apart from the above results, suggests that they cannot be formed by union molecule for molecule as it is difficult to imagine the two so widely separated carbonyl groups being associated with the auxiliary valencies of the one tin atom. Further, similar results were

obtained with other compounds: methyl and ethyl fumarates yield stannic chloride *additive* compounds of m. p. 91—92° and 81—82°, respectively; methyl and ethyl maleates yield similar, but quite distinct, compounds, m. p. 123° and 114—115°, respectively. These substances regenerate the parent ester unchanged when treated with water; the formation of the additive compounds is therefore independent of the configuration and is not the result of intramolecular change. A molecular-weight determination on the ethyl fumarate compound confirmed the formula

$$[C_2H_2(CO_2Et)_2,SnCl_4]_2.$$

Similar *compounds* are formed by methyl phthalate (m. p. 146°), methyl *iso*phthalate (needles, m. p. 71°), methyl terephthalate (m. p. 137°), and ethyl terephthalate (m. p. 65°). α-Stilbenediol diacetate yields a *compound*, m. p. 122° (decomp.), the β-isomeride a different *compound*, m. p. 98°; and the *cis*- and *trans*-forms of dibenzoylethylene both give analogous *compounds*, that from the former being very unstable, and that from the latter having m. p. 120° (decomp.).

Stannic chloride has the normal molecular weight in ethyl malonate, succinate, or glutarate and the compound of stannic chloride and ethyl oxalate is completely dissociated in these solvents.

Analogous *compounds* are formed by stannic bromide; thus, with methyl malonate, leaflets, m. p. 69°; with methyl adipate, m. p. 45°; ethyl maleate, scales, m. p. 35—36°; methyl phthalate, m. p. 20°. Similar observations to those described above were made on these compounds.

Both ethyl fumarate and maleate combine with antimony pentachloride, the *compounds*, $C_2H_2(CO_2Et)_2,2SbCl_5$, having m. p. 140° (decomp.) and 120°, respectively. The analogous *compound* from ethyl terephthalate forms leaflets.

Certain other observations are recorded, for details of which the original should be consulted. W. A. S.

Biochemistry.

Gas and Electrolyte Equilibria in the Blood. VII. Effect of Carbon Monoxide on Acidity of Hæmoglobin. A. B. HASTINGS, J. SENDROY, jun., C. D. MURRAY, and M. HEIDELBERGER (*J. Biol. Chem.*, 1924, **61**, 311—335).—The experiments on the base-binding power of oxygenated and reduced hæmoglobin (this vol., i, 1008) have been extended to carbon monoxide–hæmoglobin, which was found to behave identically with oxyhæmoglobin. Electrometric titration curves for reduced hæmoglobin and carbon monoxide–hæmoglobin over the range p_H 6·2—8·6 have been obtained. It is concluded that the increase in base-binding power of hæmoglobin, which occurs to the same extent on combination

with either oxygen or carbon monoxide, is due to an increase in the dissociation constant of one labile carboxyl group in the hæmoglobin molecule. C. R. H.

Protein Coagulation in Drops. V. Influence of Genus, Sex, and Age of Animals on the Precipitability of the Blood-serum. E. Přibyl, V. Šuk, and J. Zlámal (*Biochem. Z.*, 1924, **148**, 529—540).—The precipitability of horse, ox, and pig sera by various reagents (formaldehyde, alcohol, acids, various metallic salts, pyrogallol, tannin) differs in type and in range as studied by Bečka's drop method, and shows further variations with the age and sex of the animal. The sera of castrated animals are less readily precipitated than is the serum of normal animals. J. P.

Protein Coagulation in Drops. VI. Influence of Nitrogen Compounds on the Precipitation. J. Bečka and A. Šimánek (*Biochem. Z.*, 1924, **149**, 150—157).—Amino-acids inhibit, urea increases the precipitating action of copper sulphate on 1% horse-serum solutions; 1% ox-serum is more readily precipitated by cupric, zinc, and ferrous salts in the presence of amino compounds than in their absence. The action of the amino group in these respects is not affected by alterations in the concentration of the protein or of the sodium chloride present. The action of amino nitrogen in increasing the precipitation of horse-serum by tannin can be utilised for the detection of the former in dilutions as great as $M/10{,}000$. J. P.

Chlorides of Serum, Blood, and Corpuscles in Pathological Conditions. H. C. Gram (*J. Biol. Chem.*, 1924, **61**, 337—343).—A study of cases of various diseases shows that a deviation from the normal in the concentration of chloride in the serum is accompanied by a corresponding percentage deviation in the chloride of the whole blood; assuming that corpuscle chlorides vary directly with serum chlorides, it is possible to calculate the chloride concentration of the whole blood from that of the serum together with a determination of the corpuscle volume. The observed results agree with those calculated in this manner to within 3%. C. R. H.

Refractometric and Interferometric Quantitative Analysis. II. Blood-serum. J. Bečka (*Z. physiol. Chem.*, 1924, **139**, 52—56).—When serum is mixed with dilute sodium chloride, the refraction of the mixture is usually smaller than that calculated. The deviations from the calculated value differ with different species and depend on the age of the animal from which the serum was obtained and also on the age of the serum itself. E. S.

Refractometric and Interferometric Analysis. III. Changes in the Refractive Power of Serum. J. Bečka and V. Zemanec (*Z. physiol. Chem.*, 1924, **139**, 97—106).—Under the influence of carbon dioxide, warmth, and light, the refractive index of sterile serum is increased on standing for 24 hours; in presence of oxygen, it is diminished; these changes are greater in ox-serum

than in horse-serum and are more rapid in the serum of young than of old animals. C. R. H.

Surface Tension of Serum. X. Thickness of a Unimolecular Layer of Serum. P. L. Du Noüy (*J. Exp. Med.*, 1924, **40**, 133—149; cf. this vol., i, 900).—Consideration of the minimum value of the surface tension in relation to the dilution of a serum solution leads to the supposition that a unimolecular layer exists at a certain dilution. The thickness of the protein molecule is then calculated to be $35{\cdot}4\times10^{-8}$ cm. The result for crystalline egg-albumin was $52{\cdot}8\times10^{-8}$ cm. Chemical Abstracts.

Nature of Blood-sugar. W. Denis and H. V. Hume (*J. Biol. Chem.*, 1924, **60**, 603—612).—In a repetition of the work of Winter and Smith (A., 1923, i, 513), the authors have failed to observe any decrease in the power of normal blood filtrates on keeping for 3 days to decolorise permanganate. Although changes in the rotatory power of such filtrates have been occasionally observed, these have always coincided with the growth of mould in the polarimeter tube and have never occurred when sodium or potassium fluoride has been used as anti-coagulant. Thus no support is given to the view that γ-glucose is present in normal blood. E. S.

Blood-sugar and Gastric Hunger Contractions. E. Bulatao and A. J. Carlson (*Amer. J. Physiol.*, 1924, **69**, 107—115).—Intravenous injection of dextrose inhibits gastric hunger contractions which, in insulin hypoglycæmia, increase at a blood-sugar concentration of 0·07—0·08%. Dextrose, but not lactose, inhibits the gastric tetany of hypoglycæmia. A. A. E.

Hypoglycæmia and Acidosis. F. B. Talbot, E. B. Shaw, and M. E. Moriarty (*J. Amer. Med. Assoc.*, 1924, **83**, 91—93).—Acidosis during fasting is accompanied by low blood-sugar concentrations (45 mg. per 100 c.c.). A certain proportion of the fatty acids is not completely oxidised, and the keto-acids thus produced deplete the alkali reserve; this is accompanied by a shift of the p_H of the blood towards the acid side. The administration of carbohydrate frees the body from an excess of acids by completing the combustion of the ketone substances. Chemical Abstracts.

Lead. IX. Solubility of Various Lead Compounds in Blood-serum. L. T. Fairhall (*J. Biol. Chem.*, 1924, **60**, 481—484).—Determinations have been made of the solubilities of various lead compounds in blood-serum at 25°. Whilst the values obtained for lead salts (carbonate 0·0333, sulphate 0·0437 g.p.l.) do not differ greatly from the corresponding solubilities in water, that for lead monoxide is distinctly greater (1·1520 g.p.l. against 0·0171 g.p.l. in water at 20°). Metallic lead has a solubility in blood-serum of 0·578 g.p.l. at 25°. Saturation of the serum with carbon dioxide decreased the value for lead to 0·1930, but produced no marked effect on the other solubilities. The results are of significance as indicating the ease with which lead oxides can enter the circulation from the respiratory tract. E. S.

Effect of Ultra-violet Light on the Condition of Calcium in the Blood. J. H. CLARK (*Amer. J. Hyg.*, 1923, **3**, 481—482).—The diffusible calcium of blood-serum, measured by dialysis in collodion sacs against physiological saline, was found to be higher after the serum was exposed to radiation of a quartz-mercury arc. The diffusible calcium in rabbit-serum rose from 38 to 58%, in dog-serum from 44 to 53%. CHEMICAL ABSTRACTS.

Creatinine in the Blood. P. FONTEYNE and P. INGLEBRECHT (*Ann. med.*, 1923, **14**, 470).—The creatine and creatinine content of the blood was determined in 100 healthy and sick subjects. The coefficient of secretion of creatinine remains longer intact than Ambard's ureosecretory coefficient. The amount of creatinine in the blood is comparatively independent of the diet.
CHEMICAL ABSTRACTS.

Chemistry of the Blood during Pregnancy. H. J. STANDER (*Bull. Johns Hopkins Hosp.*, 1924, **35**, 133—137).—In non-pregnancy and pregnancy, respectively, 100 c.c. of blood contained, in mg.: non-protein nitrogen, 32, 28; urea nitrogen, 18·5, 12·48; uric acid, 3·3, 3·3; carbon dioxide combining power of plasma, 52, 44·5; ratio of urea nitrogen to non-protein nitrogen, 57, 44·5.
CHEMICAL ABSTRACTS.

Enzyme Content of the Blood. II. Variations in the Catalase and Protease Figures during 24 Hours in Animals and Man. E. IVANITZKY-VASSILENKO and A. BACH (*Biochem. Z.*, 1924, **148**, 469—473).—Extreme daily variations in the blood catalase values are: in rabbits +33%, −10%; in cats +18%, −10%; in man +9%, −9% of the mean values in each case. The protease content shows wide variations up to ±100% of the mean. J. P.

Enzyme Content of the Blood. III. Catalase Values of the Blood of Thyroidectomised Goats. A. BACH and E. CHERASKOVA (*Biochem. Z.*, 1924, **148**, 474—475).—Thyroidectomy has no influence on the mean blood catalase value in goats.
J. P.

Eosinophile Granule Substance of the Blood and its Preparation, Nature, and Properties. I. Technique of Isolation. A. NEUMANN (*Biochem. Z.*, 1924, **148**, 524—528).—The isolation of the eosinophile granule substance from horse-blood fibrin is described. This substance is characterised by an intense benzidine peroxydase reaction and is very resistant to the action of acids and alkalis. J. P.

Animal Calorimetry. XXV. Relative Specific Dynamic Action of Various Proteins. D. RAPPORT [with J. EVENDEN] (*J. Biol. Chem.*, 1924, **60**, 497—511).—The specific dynamic action of a number of proteins (beef, casein, gliadin, codfish, chicken, gelatin) has been found to be approximately the same despite the large differences in their amino-acid composition. The addition of cystine to gelatin, which, it was considered, might lead to the

production of glutathione in the organism, did not increase the specific dynamic action of this protein. E. S.

Animal Calorimetry. XXVI. Inter-relations between certain Amino-acids and Proteins with Reference to their Specific Dynamic Action. R. Weiss and D. Rapport [with J. Evenden] (*J. Biol. Chem.*, 1924, **60**, 513—544).—Although the specific dynamic actions of glycine and alanine, when administered simultaneously to a dog, are largely additive, the administration of glycine or alanine either orally, subcutaneously, or intravenously, simultaneously with the oral administration of protein (gelatin, casein), does not lead to a summation of effect unless the protein is fed in an amount which is small relative to the amount of amino-acid administered. The protein is apparently able to "neutralise" the action of the amino-acid. The specific dynamic actions of proteins, when fed together, are, however, additive. The authors consider it probable that certain amino-acids or polypeptides derived from the proteins combine with the glycine and so neutralise its specific dynamic effect. E. S.

Animal Calorimetry. XXVII. Administration of Various Proteins with Benzoic Acid to a Pig. F. A. Csonka (*J. Biol. Chem.*, 1924, **60**, 545—582).—When benzoic acid is included in the diet of a pig, it is eliminated in the urine in the form of hippuric acid, benzoylglycuronic acid (cf. Magnus-Levy, A., 1907, ii, 979), and free benzoic acid. The relative amounts of the two former substances excreted depend on the quantity of preformed glycine (free amino-acid or combined as protein) ingested. An increase in the latter eads to an increase in the excretion of hippuric acid and a decrease in that of benzoylglycuronic acid. Hence the equality in the specific dynamic actions of equal amounts of different proteins with varying contents of glycine (cf. preceding abstracts) does not depend on the synthesis of this amino-acid in the organism. E. S.

Animal Calorimetry. XXVIII. Respiratory Metabolism of a Young Pig as Influenced by Food and Benzoic Acid. D. Rapport, R. Weiss, and F. A. Csonka [with J. Evenden] (*J. Biol. Chem.*, 1924, **60**, 583—601).—No definite effect on the heat production of the pig is produced by the ingestion, under varied dietary conditions, of benzoic acid (hence by the synthesis of hippuric acid) or of hippuric acid. Following a starchy meal, the conversion, by the pig, of carbohydrate into fat (cf. Lusk, A., 1915, i, 614) may continue for more than 21 hours; the maximum conversion observed amounted to 77% of that theoretically possible. E. S.

Metabolism of some Pyrimidines. H. J. Deuel, jun. (*J. Biol. Chem.*, 1924, **60**, 749—763).—No pyrimidines are excreted in normal urine. When fed to dogs in single doses of 1 to 3 g., thymine and uracil are partly metabolised (as shown by the rise, which usually occurs, in urinary carbamide) and partly excreted unchanged, but when the same amounts are administered in small

doses they are completely destroyed in the organism. Following the ingestion of 50 g. of thymus-nucleic acid, the urine of a dog gave qualitative tests for pyrimidines. These results suggest that, contrary to current views, the destruction of pyrimidines contained in nucleic acid takes place after liberation from the latter. E. S.

Inorganic Metabolism. III. Significance of Phosphates in the Production of Tetany. F. P. UNDERHILL, E. G. GROSS, and W. COHEN (*J. Metab. Res.*, 1923, **3**, 679—709; cf. this vol., i, 452, 453).—Intravenous or intraperitoneal injection of sodium or potassium phosphate causes, with dogs and rabbits, a corresponding diminution of calcium. The intravenous administration of sodium hydrogen carbonate also produces tetany, but no diminution of calcium. The amount of calcium in the bones of rabbits is not affected by intravenous injection of comparatively large quantities of sodium orthophosphate. CHEMICAL ABSTRACTS.

Rate of Sugar Absorption in the Newborn. R. G. FLOOD (*J. Amer. Med. Assoc.*, 1924, **82**, 1595—1596).—The various sugars have different rates of absorption, dextrose being the most readily absorbed. The disaccharides show some of the characteristics of their component monosaccharides. Sucrose is not readily absorbed by very young infants, but the ability to utilise this sugar increases with the age of the infant. CHEMICAL ABSTRACTS.

Extraction and Precipitation of Soluble Proteins of Muscle. P. E. HOWE (*J. Biol. Chem.*, 1924, **61**, 493—522).—The concentration of a salt necessary for its maximum solvent action on muscle proteins has been shown to bear a definite relationship to the concentration of the same salt which will bring about precipitation of the blood proteins. When the solvent action of salt solutions towards muscle proteins was tested over a continuous range of varying concentrations, there were observed, for any one salt, certain zones of concentration in which the amount extracted was the same; these zones were taken to represent individual protein fractions. A method, based on this hypothesis, has been developed, whereby, using as solvent different molecular concentrations of a solution containing mono- and di-potassium phosphates in the ratio 1 : 2, it is possible to separate the proteins of muscle into six fractions. The work of Halliburton (A., 1887, 984) and of von Fürth (A., 1896, ii, 48) is reviewed in the light of this new fractionation, and details are given of the results of the method when applied to the muscles of various animals. C. R. H.

Creatine Content of Frog's Muscle during Work. I. H. SCHLOSSMANN (*Z. physiol. Chem.*, 1924, **139**, 87—94).—Stimulation of frog's muscle perfused with Ringer solution with or without the addition of creatine produces an increase in the creatine content of the muscle in the case of winter frogs but not in that of summer frogs. This corresponds with the smaller creatine content of the muscles of the former; stimulation evidently causes it to approach that of the latter. E. S.

Animal Nutrition. IV. Nitrogen, Ash, and Phosphorus Distribution in Beef Flesh. W. S. RITCHIE, C. R. MOULTON, P. F. TROWBRIDGE, and L. D. HAIGH (*Univ. Missouri Agr. Exp. Sta. Res. Bull.*, 1923, **59**, 1—78).—The ash of the fat of the rib is higher than that of the lean; total phosphorus is much higher in lean flesh than in fat. The ratio of soluble to total phosphorus increases as the animal grows thinner. The effects of age and of the plane of nutrition are investigated. CHEMICAL ABSTRACTS.

Photochemistry of the Visual Purple. S. HECHT (*J. Gen. Physiol.*, 1924, **6**, 731—740).—The velocity of bleaching of visual purple by light, under comparable conditions of concentration, volume, and surface exposed, is directly proportional to the intensity. D. R. N.

Aminogenesis in the Grey and White Substances of the Brain during Hunger. A. PALLADIN and D. ZUWERKALOW (*Z. physiol. Chem.*, 1924, **139**, 57—63).—During fasting in dogs, the coefficient of aminogenesis—*i.e.*, the amino-acid nitrogen expressed as a percentage of the total nitrogen—of the grey substance of the brain is depressed and that of the white substance increased. E. S.

Chemistry of Bull's Testicles (Extractives). L. LEIBFREID (*Z. physiol. Chem.*, 1924, **139**, 82—86).—αα-Dimethylguanidine has been isolated in the form of its chloroaurate, which was identical with that prepared by Schenck (A., 1912, i, 424). E. S.

Uric Acid Content of Human Amniotic Fluid. J. L. WILLIAMS and J. A. BARGEN (*Amer. J. Obst. Gym.*, 1924, **7**, 406).—Uric acid and creatinine are present in human amniotic fluid in greater concentration than in blood. The amounts of carbamide, non-protein nitrogen, and uric acid in the fluid increase as the term of pregnancy is prolonged. CHEMICAL ABSTRACTS.

Spinal Fluid Sugar. B. J. ALPERS, C. J. CAMPBELL, and A. M. PRENTISS (*Arch. Neurol. Psychiatry*, 1924, **11**, 653—663).—The spinal fluid dextrose normally varies from 50 to 84 mg. per 100 c.c.; average figures are given for various pathological conditions. CHEMICAL ABSTRACTS.

Natural Porphyrins. XI. H. FISCHER, H. KÄMMERER, and A. KÜHNER (*Z. physiol. Chem.*, 1924, **139**, 107—117).—The sterile autolysis of beef always gives rise to Kämmerer's porphyrin, which can be demonstrated spectroscopically after about 10 days; after 6 weeks the spectrum of coproporphyrin can also be observed. These results are similar to those previously obtained in the putrefaction of meat (this vol., i, 894). C. R. H.

Hydrogen-ion Concentration of the Cerebro-spinal Fluid of Children. K. WALTNER (*Biochem. Z.*, 1924, **149**, 145—149).—The p_H of the cerebro-spinal fluid from normal children is 7·50 to 7·55, in tuberculous meningitis it is unchanged, whilst in purulent

meningitis it may be somewhat lower. Successive fractions taken during a lumbar puncture tend to become more acidic. J. P.

Comparison of the Metabolism of some Mineral Constituents of Cow's Milk and of Human Milk. C. C. WANG and L. H. DAVIS (*Amer. J. Diseases Children*, 1924, **27**, 569—577; cf. *ibid.*, 352).—The greater intake of chlorine with cow's milk causes an increase in the excretion of chlorine. The utilisation of chlorine runs parallel to the urinary chlorine; there is no marked difference in percentage utilisation of chlorine intake between the two milks. As age increases there is a decrease in the amount of chlorine retained with cow's milk, but not with human milk.

CHEMICAL ABSTRACTS.

Reaction of the Urine of the Horse. F. PÁDÁR (*Biochem. Z.*, 1924, **149**, 200—205).—Electrometric determinations of the influence of varying carbon dioxide tensions on the reaction of horse's urine show that it behaves like a bicarbonate solution, low carbon dioxide tensions producing a much steeper relative fall in the curve of hydroxyl-ion concentration than do higher tensions.

J. P.

Gastric Secretion and the "Alkaline Tide" in Urine. R. S. HUBBARD, S. A. MUNFORD, and E. G. ALLEN (*Amer. J. Physiol.*, 1924, **68**, 207—212).—The alkaline tide was absent in the urine of individuals whose gastric juice did not contain hydrochloric acid.

A. A. E.

Uric Acid Excretion. A. E. KOEHLER (*J. Biol. Chem.*, 1924, **60**, 721—736).—Ingestion of uric acid does not appreciably raise the level of uric acid in the blood nor does it increase its excretion in the urine. After intravenous injection approximately 50% may be recovered from the urine. The amount of uric acid retained in the blood 2 hours after injection and its rate of excretion may serve as guides in determining renal insufficiency. E. S.

Origin of Urinary Ammonia. R. F. LOEB, D. W. ATCHLEY, and E. M. BENEDICT (*J. Biol. Chem.*, 1924, **60**, 491—495).—That the ammonia content of the renal venous blood of the dog is much greater than that of arterial blood (Nash and Benedict, A., 1922, i, 191) has been confirmed and it has been further found that venous blood from other sources has an ammonia content slightly greater than that of arterial blood. With an animal (rabbit) which does not excrete appreciable amounts of ammonia in the urine the ammonia content of the renal venous blood is practically identical with that of arterial blood. These results give further support to the theory of Nash and Benedict that the kidney is the seat of formation of urinary ammonia. E. S.

Variations in Rate of Excretion of Acetone Compounds. R. S. HUBBARD and F. R. WRIGHT (*J. Biol. Chem.*, 1924, **61**, 377—385).—Subjects fed on diets of which the ketogenic ratio (cf. Shaffer, A., 1922, i, 83) was between 1 : 1 and 2 : 1 showed an increased excretion of acetone compounds, although not so much as is required

by the theory that 1 mol. of antiketogenic material can bring about the combustion of only 1 mol. of ketogenic material. The rate of excretion showed considerable diurnal variations, being usually at its height soon after food and not running parallel with the rate of excretion of urine. C. R. H.

Ether Anæsthesia. III. Rôle of Lactic Acid in the Acidosis of Ether Anæsthesia. E. RONZONI, I. KOECHIG, and E. P. EATON (*J. Biol. Chem.*, 1924, **61**, 465—492).—The acidosis observed in ether anæsthesia appears, from a series of experiments on dogs, to be chiefly due to the accumulation of lactic acid derived from the tissues; in view of the loss of phosphate from the muscles during anæsthesia observed by Stehle and Bourne (this vol., i, 900), this may indicate a breakdown in the muscle of a hexosephosphate such as the lactacidogen of Embden (A., 1921, i, 528). The view of Anrep and Cannan (*J. Physiol.*, 1923—24, **58**, 244) that accumulation of lactic acid is controlled by the p_H of the blood through the tension of carbon dioxide, is not supported by the experiments. C. R. H.

Excretion of Phosphoric Acid during Anæsthesia. W. BOURNE and R. L. STEHLE (*J. Amer. Med. Assoc.*, 1924, **83**, 117—118; cf. A., 1922, i, 1085, and *J. Biol. Chem.*, 1924, **60**, 17).—Eleven of fifteen cases of surgical anæsthesia showed in consequence a definitely increased excretion of phosphorus. The effect is usually most pronounced during the anæsthesia, but with chloroform, and with ether preceded by morphine, it is later. The chloride excretion does not show any significant variations. Apparently phosphoric acid is responsible for the acidosis of anæsthesia. CHEMICAL ABSTRACTS.

Low Nitrogen Metabolism with Low Carbohydrate Diet in Diabetes. K. PETREN (*J. Biol. Chem.*, 1924, **61**, 355—363).—The total nitrogen metabolised, as indicated by the ratio, grams total urinary nitrogen : kg. body-weight, may be maintained at a very low level for prolonged periods in diabetics receiving a diet poor in protein and carbohydrate but rich in fat; this indicates that the sparing effect of fat ingestion on nitrogenous metabolism is greater than has hitherto been supposed. C. R. H.

Lipæmia. I. Micro-determination of Blood Fat. H. I. BING and H. HECKSCHER (*Biochem. Z.*, 1924, **149**, 79—82).—The blood is absorbed on filter-paper, extracted by a suitable fat solvent, and the turbidity of a solution of the fat in 99·5% alcohol, after treatment with an aqueous solution of 1% barium chloride, is compared with standard opacity suspensions in a Heckscher nephelometer (*Compt. rend. Soc. Biol.*, 1921, **85**, 378). J. P.

Lipæmia. II. Blood Fat in Normal Human Subjects. H. I. BING and H. HECKSCHER (*Biochem. Z.*, 1924, **149**, 83—89).—In 155 cases out of 213 examined, the fat content of the normal blood in a fasting condition lay between 0·05% and 0·13%. The remaining 58 cases showed values between 0·14% and 3·16%. The

incidence shows a maximum at 0·10%. The individual fasting blood-fat value remains practically constant. The blood fat reaches a maximum in from 3 to 5 hours after a meal, but the form of the blood-fat curve varies with the nature of the diet. Direct observation of the turbidity of the blood-serum is not a trustworthy indication of the fat content. J. P.

Lipæmia. III. Pathological Changes in the Blood-fat Value. H. I. Bing and H. Heckscher (*Biochem. Z.*, 1924, **149**, 90—99).—Children and young people often have blood-fat values below normal. Hypolipæmia was found in three cases of Basedow's disease, hyperlipæmia in cases of acute lung and uncompensated heart affections, in cases of icterus, in various types of nephritis, in diabetes mellitus, and in cases of disturbed endocrine function involving fat metabolism. In some cases the hyperlipæmia was latent, *e.g.*, in arthritis urica the fasting value was normal and the abnormality was revealed only after a meal. J. P.

Amino-acids in Physiological Fluids. G. Wolpe (*Münch. med. Woch.*, 1924, **71**, 363—365; from *Chem. Zentr.*, 1924, **i**, 2377).—Increased amino-acid content in the blood-serum in malaria and leucæmia is due to increased decomposition of blood proteins. There appears to be a correlation between the resistance of the organism and the amino-acid content in physiological fluids. Amino-acid production may be connected with disturbances in the endocrine glands. G. W. R.

Relation of Acidosis and Hyperglycæmia to the Excretion of Acids, Bases, and Sugar in Uranium Nephritis. B. M. Hendrix and M. Bodansky (*J. Biol. Chem.*, 1924, **60**, 657—676).—The acidosis which, together with hyperglycæmia and glycosuria, is produced in dogs by administration of uranium acetate is accompanied in the early stages by an increased excretion of basic phosphates and salts of organic acids, and in the later stages by a marked decrease in phosphate excretion. No constant relationship appears to exist between the degree of acidosis and the hyperglycæmia and glycosuria. E. S.

Chemistry of Osteohæmochromatosis in Animals. D. von Deseö (*Biochem. Z.*, 1924, **149**, 191—199).—The pigment occurring in the bones of animals with osteohæmochromatosis has chemical and spectroscopic properties which suggest that it originates from blood pigment and is possibly a hæmatoporphyrin. J. P.

Rate of Excretion of Urea in the Toxæmias of Pregnancy. H. J. Stander, E. C. Duncan, and B. L. Moses (*Bull. Johns Hopkins Hosp.*, 1924, **35**, 97—103).—Average results are given for non-pregnant, pregnant, and pathological conditions.

Chemical Abstracts.

Excretion of Tryparsamide. A. G. Young and C. W. Muehlberger (*J. Pharm. Exp. Ther.*, 1924, **23**, 461—464).—At least part of the tryparsamide is excreted unchanged in the urine and in three out of four normal individuals 88—95% of the arsenic

of the drug was excreted within the first 24 hours. Some individuals show a much slower rate of excretion, and may therefore be more susceptible to cumulative effects of the drug. D. R. N.

Test-tube Reaction for Damage and Death of Tissues. P. Rostock (*Fermentforsch.*, 1924, **8**, 72—85).—After testing the various reactions which have been proposed for distinguishing between living and dead tissues, the author concludes that the most trustworthy are the dinitrobenzene reaction of Lipschitz (*Pflüger's Arch.*, **199**) and the nitroanthraquinone reaction of Bieling (*Zentr. Bakt.*, 1923, **90**). C. R. H.

Effect of Potassium on the Acid Metabolism of Surviving Skeletal and Cardiac Muscles of the Frog. F. R. Griffith (*J. Gen. Physiol.*, 1924, **6**, 683—695).—The potassium contraction of skeletal muscle and relaxation of cardiac muscle have been correlated with the carbon dioxide and total acid production of these tissues. The immersion of surviving sartorius muscles of the frog in isotonic potassium chloride solution causes a marked increase in the rate of acid production, carbon dioxide being probably the principal acid involved. Surviving cardiac muscle treated in a similar manner shows a pronounced depression in the rate of acid production. It is believed that these changes in metabolism may be independent of the stimulation and inhibition of contraction which potassium simultaneously produces in these tissues. D. R. N.

Factors influencing Chemical Processes of Fracture Healing. R. Schwarz, R. Eden, and E. Herrmann (*Biochem. Z.*, 1924, **149**, 100—108).—Ossification after fracture consists primarily in the addition of calcium to organic substances and the secondary combination of phosphoric acid with the fixed calcium until a ratio Ca : P=1 : 0·6 is attained, at which stage the cartilage becomes ossified. J. P.

Mechanism of Phloridzin Diabetes. T. P. Nash, jun., and S. R. Benedict (*J. Biol. Chem.*, 1924, **61**, 423—428).—The fact that insulin may be obtained by the usual procedure from the pancreas of phloridzinised dogs is evidence against the view of Ringer (this vol., i, 446) that the effect of phloridzin is to injure the pancreas, rendering it unable to produce insulin. C. R. H.

Action of Quinine on Protein Metabolism, Respiratory Exchange, and Heat Function. I. Protein Metabolism. S. W. Hardikar (*J. Pharm. Exp. Ther.*, 1924, **23**, 395—448).—The view generally held that quinine diminishes heat production by lowering nitrogen metabolism is not substantiated. Quinine has no influence on protein metabolism even in doses which may be toxic in themselves. D. R. N.

Pressor Anæsthetics. C. S. Marvel and V. du Vigneaud. —(See i, 1193.)

Experiments with Anæsthetic Gases, Propylene, Methane, and Methyl Ether. W. E. Brown (*J. Pharm. Exp. Ther.*, 1924, 23, 485—496).—Propylene induces anæsthesia at a concentration as low as 37% when mixed with either oxygen or air. Anæsthesia may be maintained satisfactorily at a concentration as low as 20%. In concentrations of about 65% or higher it is poisonous. Methane produces anæsthesia only at high concentrations (87%) whilst 90% methane administered to a cat caused irregular respirations which gradually ceased. Methyl ether produces anæsthesia at concentrations of 65%; 85% causes profound anæsthesia with gradual cessation of respiration. D. R. N.

Chloroform Poisoning. H. J. Stander (*Bull. Johns Hopkins Hosp.*, 1924, **35**, 46—49).—In a fatal case of delayed chloroform poisoning there was an increased output of urinary nitrogen with a marked decrease of the urea-nitrogen % and a steadily rising ammonia coefficient; a very definite drop in the carbon dioxide-combining power of the blood to 27·4 vols. %, an increase in the blood of non-protein nitrogen, urea, uric acid, and amino-acids, and a fall in blood-sugar to 0·058%. These changes indicate an increased destruction but incomplete oxidation of the proteins.

Chemical Abstracts.

Physiological Actions of Cyanides. T. H. Bodine (*J. Gen. Physiol.*, 1924, **7**, 19—23).—The physiological action of hydrocyanic acid and its salts depends on (*a*) the ease with which hydrogen cyanide penetrates living cells as such and then ionises; (*b*) the presence of large amounts of the free acid even in the presence of cyanides; (*c*) specific effects due to chemical activity. Hydrocyanic acid in acid, neutral, or slightly alkaline media produces intracellular acidity on account of its rapid penetration into the cell. It acts specifically on certain protozoa, the resistance towards it being the reverse of that to mineral acids. O. O.

Toxicity of a Polymeride of Hydrocyanic Acid. Ch. Bedel (*J. Pharm. Chim.*, 1924, [vii], **30**, 189—193).—Dicyanomethylamine hydrocyanide, $[HCN]_4$, is much less toxic than hydrocyanic acid, the minimum lethal dose being about 0·75 g. per kg. body-weight when given by mouth. The symptoms of poisoning are similar to those of hydrocyanic acid, but sodium thiosulphate is without effect as an antidote. C. R. H.

Biochemistry of Carotinoid Pigments in Animals. L. S. Palmer (*Minnesota Agr. Exp. Sta., Ann. Rept.*, 1922, 43—44).—The yellow lipochrome of cod-liver oil is not a carotinoid and cannot be removed completely by treatment with charcoal. The yellow pigment in the blood serum of pigeons has been identified as xanthophyll. The red pigment in the feet and legs resembles carotin in its solubility, but not in other respects. Alcoholic solutions treated with lime-water yield an amorphous pigment, which gives a blue colour when treated with ferric chloride instead of a green, characteristic of carotin and xanthophyll. Human organisms lose carotinoid pigments by the process of oxidation.

Carotinoid skin colorations are due to lowered oxidation processes of the body and super-abundance of carotinoids in the diet.

CHEMICAL ABSTRACTS.

Concentration of Silver Ions in Solutions of Colloidal and Complex Silver Preparations with Special Reference to their Medicinal Use. H. SCHLEE (*Biochem. Z.*, 1924, **148**, 383—432).—Excess of sodium chloride in a solution of silver chloride diminishes the silver-ion concentration in accord with the solubility-product equation. Egg-albumin has a similar but more marked effect on solutions of silver nitrate, and this persists after the protein has been dialysed to remove naturally occurring sodium chloride. Blood-serum has a still more marked effect in diminishing the silver-ion concentration. The findings of Paul (*Z. Elektrochem.*, 1912, **18**, 521) with regard to the classification of medicinal silver preparations into three groups are confirmed. It is possible from such behaviour to draw conclusions as to the nature of the silver in these preparations. Determinations were made of the silver-ion concentration of the blood after injections of certain colloidal silver preparations.

J. P.

Photodynamic Phenomena. III. Fixation of Active Dyes in the Cell. P. METZNER (*Biochem. Z.*, 1924, **148**, 498—523).—Photodynamically active dyes show in general negative phototaxis. Cresyl fast violet exhibits induced photokinesis. In the cell, the active portion of the dye is adsorbed and shows absorption and fluorescent spectra which differ from those of the substance when in solution, being displaced towards the red. It is suggested that the active adsorbent is a phosphatide or a tyrosine compound. The activity spectra and absorption spectra are approximately proportional without showing exact correspondence, and the former is also displaced towards the red in the adsorbed dye. It is concluded that photodynamic dyes become active only within the cell.

J. P.

Permeability of Living and Dead Cells. III. Penetration of certain Alkalis and Ammonium Salts into Living and Dead Cells. M. M. BROOKS (*U.S. Pub. Health Rpts.*, 1923, **38**, 2074—2086, *Reprint No.* 866).—The rate of penetration of bases into living cells has been measured, using the marine alga, *Valonia ventricosa*, and the method previously described (cf. *ibid.*, 1923, **38**, 1449). Ammonia, ammonium chloride, sulphate, and carbonate cause an increase in the p_H of the sap of *Valonia*, due to the penetration of free ammonia. On removal of the ammonia by aëration, the p_H of the sap returns to normal. Both ions of ammonium carbonate penetrate and can be removed by aëration. Solutions of sodium and potassium hydroxides penetrate into the cell sap very much more slowly than an ammonia solution having the same p_H. Dead cells rapidly assume the p_H of the surrounding solution. The results confirm the view that the relative p_H of the sap of living cells and of the solution surrounding them is greatly influenced by the nature of the ions present in the solution.

C. T. G.

Permeability of Living and Dead Cells. IV. Penetration of Tervalent and Quinquevalent Arsenic into Living and Dead Cells. M. M. BROOKS (*U.S. Pub. Health Rpts.*, 1923, **38**, 2951—2966, *Reprint No.* 888).—Determinations have been made of the amount of arsenic passing from surrounding solutions into the sap, protoplasm, and cell-wall of *Valonia* (cf. preceding abstract). Arsenic, whether in the quinquevalent form (as As_2O_5 and atoxyl) or in the tervalent form (as As_2O_3), penetrates least when the solution is nearly neutral. With increasing alkalinity or acidity more arsenic is taken up. Tervalent arsenic, from acid solutions, penetrates less readily into the protoplasm but more readily into the sap than quinquevalent arsenic; in alkaline solutions, the behaviour of the two forms is similar. Previous exposure of the cells in sodium hydrogen carbonate solution (when carbon dioxide accumulates in the sap) increases by 150% the quiquevalent arsenic and reduces by 25% the tervalent arsenic taken up by protoplasm; on the other hand, the tervalent arsenic taken up by the sap is increased by about 100% and the quinquevalent arsenic only by about 25%. Penetration of arsenic into dead cells is much more rapid than into living cells. The use of phosphate buffer solutions to maintain a constant p_H sometimes led to untrustworthy results.

C. T. G.

Formation of Pigment. I. Enzymic Pigment Formation as an Aid to Classification. H. SCHMALFUSS (*Fermentforsch.*, 1924, **8**, 1—41, 86—115). **Formation of Pigment. II.** H. SCHMALFUSS and F. WERNER (*ibid.*, 116—134).—The formation of pigment from *l*-α-amino-β-3 : 4-dihydroxyphenylpropionic acid (called for brevity the "D-reaction") by an enzyme from caterpillar's blood, is increased by the presence of oxygen; nitrogen, hydrogen, acetylene, carbon monoxide and dioxide, and nitrous oxide are indifferent, whilst sulphur dioxide, hydrogen sulphide, hydrocyanic acid, cyanogen, chlorine, bromine, and ammonia inhibit the reaction. The effect of other organic substances, both alone and in presence of "D," on pigment formation by this enzyme was tested in a large number of cases. The substances investigated fell into four groups, according to whether or not they inhibited the formation of pigment from "D," and whether or not they could themselves act as precursors of pigment. The application of these criteria made it possible in many instances to distinguish between isomerides, *e.g.*, between *o*-, *m*-, and *p*-cresol. Formation of melanin could be demonstrated when strips of filter-paper, previously treated with a solution of egg-albumin in strong potassium hydroxide, were immersed in solution either of "D" or of pyrocatechol.

The above experiments were extended to enzyme preparations derived from the body fluids of a number of different animal species; by the application of the same criteria a series of results was obtained which, it is claimed, may form a useful support to morphological grounds of classification.

Although in the case of the precursor "D" the formation of pigment by the enzyme from caterpillar's blood is very much

accelerated by oxygen, the effect of the latter with other precursors is less marked. The reaction does not take place in anhydrous solvents and is not affected by light. The effect of heat shows that two active agents are involved, one heat-labile, which reaches its optimum at 40° and is inactivated at 70°, and the other heat-stable, which increases in activity up to 100°. The enzyme is destroyed by acids and inhibited by bases. Preparations from caterpillar's blood become more active with keeping, both as regards catalase and oxydase, but both fresh and old preparations are destroyed with equal ease by dilute sulphuric acid. C. R. H.

Investigation of Amylase. P. Rona and C. van Eweyk (*Biochem. Z.*, 1924, **149**, 174—187).—A method for investigating amylolytic activity is described in which glycogen is used as the substrate, its concentration being determined continuously throughout the course of the reaction by means of the nephelometer. J. P.

Amylase. K. Sjöberg and E. Eriksson (*Z. physiol. Chem.*, 1924, **139**, 118—139).—Amylase from barley after germination can carry the hydrolysis of starch further than that obtained before germination; with the most active amylase, however, there could not be obtained a greater yield of maltose than 80%. Separate experiments with amylose and amylopectin as substrates showed that these substances individually were hydrolysed to the extent of 80% also. The affinities of the enzyme for amylose and amylopectin are of the same order of magnitude, but not identical. The inhibiting effects of maltose and dextrose are different according to whether they are measured by the rate of maltose production or by the rate of disappearance of the iodine reaction. This supports the hypothesis that two enzymes are concerned in the hydrolysis of starch by amylase. C. R. H.

Antiamylase. H. Lüers and F. Albrecht (*Fermentforsch.*, 1924, **8**, 52—72).—The serum of rabbits which have been injected subcutaneously with preparations of amylase contains a substance which inhibits the action of the enzyme; such serum also gives a precipitin reaction with solutions of the amylase injected. These reactions are in a high degree specific to the particular amylase employed. The anti-body to the enzyme is stable when heated at 56°. After the injection of amylase, previously inactivated by heat, the precipitin reaction is still obtained, but the serum has no inhibitory action towards the enzyme. There are therefore involved two distinct immunity reactions, the production of an anti-body to the enzyme itself, and of another to the protein which accompanies it. C. R. H.

Relation between Catalase and Autoxidisable Substances. D. Rywosch (*Fermentforsch.*, 1924, **8**, 48—51).—The presence of catalase in the body fluids of invertebrates has been demonstrated to run parallel with the presence therein of an autoxidisable chromogen. C. R. H.

Stability of Yeast Catalase. K. Nakamura (*Z. physiol. Chem.*, 1924, **139**, 140—146).—The observed rate of inactivation of

yeast catalase during autolysis of yeast is about 20,000 times greater than can be accounted for by the effect of temperature alone; this is apparently due to the presence of enzymes which destroy catalase. C. R. H.

Rôle of the Mineral Constituents in Plants. I. Influence of Neutral Salts on Catalase. A. J. SMIRNOV and S. P. ALISSOVA (*Biochem. Z.*, 1924, **149**, 63—78).—The reaction of aqueous extracts of wheat containing naturally occurring buffer salts is not altered by the addition of the chlorides of univalent metals, whilst the chlorides of the bivalent metals lower the p_H by 0·2 to 0·6. By increasing the p_H from 3·5 to 7·3, the relative activity of the catalase present increases from 4·76 to 135·98. Bivalent cations inhibit the activity of catalase twice as strongly as univalent cations, whilst a similar relation between inhibitory power and valency is not observed in the case of the anions, the series being $SO_4 < PO_4 < Cl < NO_3$ in the order of increasing inhibition. Univalent cations are active in concentrations of $M/320$, bivalent cations at $M/640$. At still greater dilutions down to $M/5120$, a zone of very weak or of no inhibition is followed by one at which the inhibition again appears. J. P.

Influence of Culture of Yeast on Galactose on its Power of Fermenting this Carbohydrate. E. ABDERHALDEN (*Fermentforsch.*, 1924, **8**, 42—47).—The fact, previously recorded by other observers, that yeast, grown in a medium containing galactose, acquires an increased power of fermenting this carbohydrate, has been confirmed; similar results were obtained with the maceration juice of yeast so treated. No evidence could be obtained of increased permeability of the yeast-cells to galactose. It is suggested that, prior to fermentation, galactose must be transformed into dextrose or lævulose, and that suitable conditions for such a transformation are established in the cells by the presence of galactose in the culture medium. C. R. H.

Fermentation Co-enzyme (Co-zymase) of Yeast. V. The Rôle of the Co-enzyme in Fermentation. H. VON EULER and K. MYRBÄCK (*Z. physiol. Chem.*, 1924, **139**, 15—23).—A parallelism, which is not disturbed by variations in the co-enzyme content of the yeast, has been found to exist between the evolution of carbon dioxide and the esterification of phosphates during the fermentation of dextrose by yeast. It is concluded that the co-enzyme takes part in the formation of the hexosediphosphate or perhaps in an earlier transformation of the sugar. E. S.

Dependence of Alcoholic Fermentation on Acidity. K. MYRBÄCK (*Z. physiol. Chem.*, 1924, **139**, 30—38).—A comparison has been made between the conditions of activity of a bottom yeast, with which esterification of phosphates (decrease of free phosphates) accompanied fermentation, and a top yeast, which produced no detectable decrease in free phosphates; dry preparations were used in each case. No essential difference was found between the velocity–p_H curves. From this result, together with the effect of

phosphates on the course of the fermentation, it is concluded that the two yeasts differ only in the rate at which they decompose hexosephosphates; this rate is small with the bottom yeast and hence an accumulation of hexosephosphates occurs. E. S.

Rotation of the Maltose produced by Fermentation of Starch by Malt Extract. H. VON EULER and K. HELLEBERG (*Z. physiol. Chem.*, 1924, **139**, 24—29).—Preliminary experiments indicate that the maltose so produced contains a preponderating amount of the β-form. E. S.

Enzymic Methylglucoside Equilibrium. H. VON EULER and K. JOSEPHSON (*Arkiv Kem., Min., Geol.*, 1924, **9**, No. 7, 1—8).—For the reversible enzymic hydrolysis of β-methylglucoside, represented by the equation [β-methylglucoside–enzyme]+[water] $\rightleftharpoons$ [glucose–enzyme]+[methyl alcohol], there exist the equilibria [methylglucoside–enzyme]/[methylglucoside] . [enzyme]$=K_1$ and [glucose–enzyme]/[glucose] . [enzyme]$=K_2$. The velocity equations are, for the hydrolysis of the glucoside, $v_1=k_1$[glucoside–enzyme] . [water] and for the synthesis, $v_2=k_2$[glucose–enzyme] . [alcohol]. The progress of the reaction in the system, glucoside–glucose–alcohol–water–enzyme is hence determined by the expression, $dx/dt=v_1-v_2=k_1$[glucoside–enzyme] . [water]$-k_2$[glucose–enzyme] . [alcohol]$=k_1K_1$[glucoside] . [enzyme] . [water]$-k_2K_2$[glucose] . [enzyme] . [alcohol]. For a condition of equilibrium, $dx/dt=0$, and hence

$$k_1/k_2=K_2[\text{glucose}] \cdot [\text{alcohol}]/K_1[\text{glucoside}] \cdot [\text{water}]=K.$$

Only when $K_1=K_2$ can the position of equilibrium in this system coincide with that in the corresponding non-enzymic system.

Bourquelot (*J. Pharm. Chim.*, 1914, [vii], **10**, 361) has shown that the same equilibrium position is arrived at in the hydrolysis as in the synthesis of β-methylglucoside in presence of emulsin. By means of Bourquelot's results, the authors show that the value of K_1 in the expression, [methyl alcohol][glucose]$=K_1$[water][glucoside] remains practically constant at 0·25 for concentrations of the alcohol not exceeding about 50% and afterwards gradually rises, probably owing to increasing inactivation of the enzyme, this altering the final state and resulting in a false equilibrium. Thus, according to the theory outlined above, the affinity of β-glucosidase for glucose is about four times as great as that for methylglucoside, whereas the value of the equilibrium constant derived from the velocities of the two reactions should be 1. The affinities between the β-methylglucosidase used by Bourquelot and the reacting substances are not known, but for the emulsin employed by Willstätter, Kuhn, and Sobotka (A., 1923, i, 1034; see also Kuhn, A., 1923, i, 589; Willstätter and Kuhn, A., 1923, i, 721), the ratio between such affinities is calculated to be 3·3, which differs but little from the value 4 for the different preparation of enzyme used by Bourquelot. T. H. P.

Blood Diastases. I. S. J. COHEN (*Amer. J. Physiol.*, 1924, **69**, 125—131).—Since hyperglycæmia produced by adrenaline or

morphine, but not by ingestion of carbohydrate, and hypoglycæmia produced by insulin are associated with a fall in the blood diastase and an increase in the liver-tissue diastase, it is suggested that the function of the blood diastases is to assist in the breaking down of glycogen, and to be available for mobilisation to the organs where there is immediate need for their action. A. A. E.

Enzyme Action. XXVIII. Spontaneous Increase in the Activities of Lipase and Protease of Tissue Extracts. (Miss) H. M. Noyes, K. Sugiura, and K. G. Falk (*J. Amer. Chem. Soc.*, 1924, **46**, 1885—1889; cf. A., 1923, i, 872).—The tissues investigated were whole rats (3½ and 22 days old), rabbit liver, lung, and muscle, mouse carcinoma, and human fibromyoma of uterus. They were ground up, extracted with water, and the filtered extracts tested for lipase and protease immediately and at intervals after standing at the ordinary temperature in the presence of toluene. The lipase was determined by adding 3·4 milli-equivalents of ten different esters to 15 c.c. portions of the extracts, incubating at 37° for 22 hours, and then titrating with 0·1*N*-sodium hydroxide. For the protease actions, 0·1 g. portions of peptone, casein, and gelatin were added to the extracts to be tested and titrated by the formol method after similar incubation. The mixtures were all brought to p_H 7·0 initially. In the lipase experiments spontaneous increases were observed with some tissues and substrates and not with others. Spontaneous increases in protease action usually occurred with casein, and not with the other two substrates. A. C.

Application of Folin's Method for the Determination of Amino-nitrogen to Peptic Digestion. Y. Uwatoko (*Z. physiol. Chem.*, 1924, **139**, 76—81).—No increase in amino-acid nitrogen occurs during the digestion of casein or glycine anhydride with pepsin. Some ammonia is produced from the casein, but this is also formed by treatment with 1% hydrochloric acid at 37° alone. E. S.

Kinetics of Trypsin Digestion. J. H. Northrop (*J. Gen. Physiol.*, 1924, **6**, 723—729).—The rate of digestion of concentrated casein solutions with small amounts of trypsin has been followed with a view to prove the validity or otherwise of Schutz's rule, according to which the amount of hydrolysis should be proportional to the square root of the product of the time into the enzyme concentration. Neither Schutz's rule nor Arrhenius' equation holds accurately owing to the incorrectly assumed relation between the rate of hydrolysis and the substrate concentration. D. R. N.

Enzymic Action of Extracts of the Duodenal Region of Domestic Animals. H. D. Bergman, H. H. Dukes, and J. H. Yarborough (*J. Amer. Vet. Med. Assoc.*, 1924, **65**, 313—326).—Extracts were made from the duodenal substance of the horse, ox, sheep, and pig. The extracts invariably contained an amylolytic enzyme active in neutral solution. This action was greater than that of extracts of the submucosa of these regions,

leading to the belief that the duodenal cells themselves produce amylase. Protease and lipase were generally not found.

CHEMICAL ABSTRACTS.

Nucleosidases. I. General Properties. P. A. LEVENE, M. YAMAGAWA, and I. WEBER (*J. Biol. Chem.*, 1924, **60**, 693—706).—The kinetics of the decomposition of adenosine by nucleosidase have been investigated. Solid preparations of the enzyme were obtained by extracting the minced organs (spleen, kidney) with a phosphate buffer solution (p_H 7·0) and pouring the press-juice, after concentration, into a large volume of acetone. These, however, rapidly lost their activity; hence the press-juice was mostly employed without further purification. The optimum conditions for the action of nucleosidase are at p_H 7·5 and 37°, although irreversible inactivation occurs at much lower temperatures. With a relatively large excess of enzyme, the reaction follows the unimolecular law; deviations from this law are considered to be due to the formation of the complex enzyme–inhibitor, but attempts to calculate the dissociation constant of the latter yielded values which differed with different enzyme preparations. Both products of the reaction (adenine, ribose) exert an inhibitory action; the effect of ribose is twice that of adenine. E. S.

Nucleosidases. II. Purification of the Enzyme. P. A. LEVENE and I. WEBER (*J. Biol. Chem.*, 1924, **60**, 707—715).—The nucleosidase was extracted by suspending the washed and ground organs (2·2 kg.) in a phosphate buffer solution (4 litres) at p_H 7·0, allowing them to autolyse for 24 hours at 40°, and filtering. When kidneys were employed, the activity of the extract was increased by digesting the filtrate for a further 24 hours at 40°; with pancreas this further digestion produced inactivation. Purification was effected by fractional precipitation with colloidal iron and alcohol. Addition of 20% (by volume) of iron solution and 20% of alcohol removed the inhibitory substances; the further addition to the filtrate of 40% of iron solution and 40% of alcohol (95%) completely precipitated the enzyme. The latter was extracted from the adsorbate by disodium phosphate or sodium hydroxide at p_H 8·7. After filtration from the iron, the extract was neutralised, concentrated under diminished pressure, and the enzyme precipitated by a large excess of acetone. The solid preparation so obtained retained its activity for 10 months. It contained large amounts of inorganic material (76% ash) which could not be removed by dialysis without disappearance of the enzyme. Further purification could sometimes be effected by bringing a solution of this preparation to p_H 1·2 by addition of hydrochloric acid, when a highly active product separated as a flocculent precipitate (ash 8%); this method was not, however, invariably successful. The most active preparation gave a pink biuret reaction, but no distinct reaction with Millon's reagent; it did not reduce Fehling's solution. Nucleosidase is adsorbed by kaolin, but not by aluminium hydroxide; in the former case, the adsorbate possesses the whole of the original activity, but the enzyme cannot be recovered. E. S.

Nucleosidases. III. Degree of Specificity of Nucleosidase and Distribution of it in Various Organs and in Various Species. P. A. LEVENE and I. WEBER (*J. Biol. Chem.*, 1924, **60**, 717—720).—The optimum acidity for the decomposition of inosin by nucleosidase is identical with that for adenosine (cf. preceding abstracts). Nucleosidase is absent from dog's pancreas and from pancreatic and intestinal juices, but is present in the pancreas of cattle. It has no action on adenine hexoside.

E. S.

Action of Antiphenolase in an Adsorbed Condition. W. ENGELHARDT (*Biochem. Z.*, 1924, **148**, 463—468).—Antiphenolase, together with the serum proteins, is adsorbed from immune sera by ferric and aluminium hydroxides, charcoal, and kaolin. The adsorption is practically irreversible, and the adsorbed enzyme retains undiminished its specific affinity for phenolase in the cases of the first three adsorbents, whilst its activity is but slightly diminished in the case of kaolin.

J. P.

Coagulating Property of Papain. L. ROSENFELD (*Biochem. Z.*, 1924, **149**, 158—173).—Papain solution precipitates an aqueous solution of the mucilage prepared from the seeds of *Cydonia*. Pepsin, trypsin, rennin, and plant protease do not precipitate the mucilage. The specific affinity of papain for *Cydonia* mucilage is such that the latter may be identified and separated from mixtures with other similar substances. *Cydonia* mucilage carries a negative charge whilst papain is positive. The precipitation is therefore explained on physical grounds. The precipitate consists of both constituents and separation is difficult, although the precipitated enzyme is still capable of coagulating milk. Alkalis, inorganic acids, neutral salts, and the globulin of blood-serum inhibit the action of papain, whilst organic acids have the opposite effect. Papain also coagulates agar-agar.

J. P.

Milk-coagulating Enzyme of *Solanum elæagnifolium*. A. BODANSKY (*J. Biol. Chem.*, 1924, **61**, 365—375).—The chymase obtained from the berries of the above plant acts best at 80—85° and is more stable to heat than rennin from animal sources; the preparation showed no change in activity after dialysis; with boiled milk, coagulation takes place in some cases only. The time of coagulation is inversely proportional to the amount of enzyme present.

C. R. H.

Soluble Enzymes of the Bryony Root (*Bryonia dioica*). N. F. GIRARDET (*J. Pharm. Chim.*, 1924, [vii], **30**, 75—81).—Amylase, invertase, and peroxydase have been found in the root. It also contains a characteristic enzyme which acts on one or more of its constituents producing a dextrorotatory sugar. Basic ammoniacal lead acetate, but not neutral lead acetate, precipitates this enzyme.

D. R. N.

Utilisation of Dextrose in Mineral Media by Bacteria with reference to Acid Formation. J. S. JOFFE and H. J. CONN (*Abstr. Bact.*, 1924, **8**, 10—11).—In inorganic media with

Influence of Insulin on the Dextrose-fermenting Action of *Bacillus coli*. G. McGuire and K. G. Falk (*J. Biol. Chem.*, 1924, **60**, 489—490).—No influence was observed. E. S.

Fat-soluble Vitamins. XVII. Induction of Growth-promoting and Calcifying Properties in a Ration by Exposure to Ultra-violet Light. H. Steenbock and A. Black (*J. Biol. Chem.*, 1924, **61**, 405—422).—Food free from vitamin-*A* can be activated by exposure to the light of a mercury vapour lamp and is not subsequently inactivated by heating at 96°; muscle and liver from rats which have been exposed to ultra-violet light contain vitamin-*A*, whereas from non-irradiated animals these tissues do not contain this vitamin. C. R. H.

Concentration of Vitamin-*B*. P. A. Levene and B. J. C. van der Hoeven (*J. Biol. Chem.*, 1924, **61**, 429—443).—A series of attempts was made to concentrate vitamin-*B* by precipitation or adsorption with various reagents and subsequent recovery from the precipitate, using as starting material the fraction prepared according to Osborne and Wakeman (A., 1920, i, 208). Adsorption with kaolin was unsuccessful. A slight purification was effected by adsorption with Lloyd's reagent and subsequent extraction with alkali (p_H 9·0), also by precipitation with barium hydroxide and subsequent removal of barium with sulphuric acid. The best result was obtained by adsorption with silica gel; from the adsorbate the active material could be partly extracted at p_H 3·0, a larger and more active fraction being obtained by further extraction at p_H 9·0. C. R. H.

Spinacin, a New Protein from Spinach Leaves. A. C. Chibnall (*J. Biol. Chem.*, 1924, **61**, 303—308).—By the application of the author's method (A., 1923, i, 635) for the extraction of cytoplasmic material from leaf-cells, a new protein, "spinacin," has been isolated from the common spinach. The substance is free from carbohydrate, is insoluble in water and neutral salt solutions, but readily soluble in a small excess of either acid or alkali; it is precipitated by salts from either solution, more readily from the acid one; its isoelectric point lies between p_H 4·0 and 4·6. C. R. H.

Biochemical Hydrolysis of Rutin. Presence of Rutin in Plants and Identification of the Glucoside and its Hydrolysis Products. C. Charaux (*Bull. Soc. Chim. biol.*, 1924, **6**, 631—640, and 641—647).—A list of plants from which rutin may be extracted is given. The pure glucoside, $C_{27}H_{30}O_{16}$, crystallises from water in fine needles with $2H_2O$, and melts indefinitely at 188—190°. On heating on the water-bath with 4% sulphuric acid, an insoluble precipitate was obtained which was identified by means of its bromo derivative as quercetin. The acid mother-liquor, after removal of the quercetin, yields rhamnose and dextrose. Partial hydrolysis of rutin was brought about by an enzyme from the seeds of *Rhamnus utilis*; in this experiment the carbohydrate part of the molecule was obtained as a disaccharide ("rutinose")

which was slightly dextrorotatory, softened at 140°, and melted at 189—192° (decomp.), giving dextrose and rhamnose on acid hydrolysis. C. R. H.

Glucoside Hydrolysable by Emulsin in the Genera, *Veronica, Euphrasia, Odontites, Bartsia,* and *Pentstemon.* M. BRAECKE (*Bull. Soc. Chim. biol.*, 1924, **6**, 665—671).—Observations of the effect on the optical rotation and the reducing power of extracts of these plants brought about by emulsin show that they all contain glucosides hydrolysable by this enzyme. Invertase has, in most cases, no effect on the extracts. C. R. H.

Solanine Content of Potatoes. C. GRIEBEL (*Z. Unters. Nahr. Genussm.*, 1924, **47**, 436—408).—In many parts of Germany the potatoes grown during the year 1922 contained an unusually large quantity of solanine (0·038 to 0·079%) and their consumption caused illness; when re-grown during 1923, these potatoes produced tubers of normal solanine content (0·005%). Experiments showed that the quantity of solanine in potatoes may be doubled by exposing the latter to light for 4 days, and it would appear that the poisonous potatoes had been unduly exposed during the harvest, transport, or storage. W. P. S.

Constituents of *Astragalus sinicus*, L. K. YOSHIMURA and S. FUJISE (*J. Chem. Soc. Japan*, 1924, **45**, 32—41).—The fresh grass contained: water, 90·17%; protein, 2·19%; ether extract, 0·60% (fats, 0·25%, and colouring matters, 0·35%); fibre, 2·66%; soluble non-nitrogenous compounds, 3·41%, and ash, 0·97%. From an aqueous extract of 40 kg. of the grass, the following organic compounds were isolated: malonic acid, 2·7 g.; adenine hydrochloride, 1·5 g.; histidine, trace; arginine nitrate, 0·3 g.; choline chloroaurate, 1·5 g.; trigonelline hydrochloride, 0·12 g. No betaine was found. K. K.

Constituents of "Hang-ge." S. NAKAYAMA (*J. Pharm. Soc. Japan*, 1924, No. 509, 551—564).—The drug "Hang-ge" (Chinese: Pwan-hia) is the root nodule of *Pinellia tuberifera*, Ten., and is used as an anti-emetic. The powdered material was extracted first with ether, then with alcohol, and finally with water. The ethereal extract (1·02—1·10% of the fresh material) is composed of an ethereal oil and a fatty oil (semi-solid in ordinary temperature, iodine value 80·92, saponification value 133·32, acid value 1·91). On hydrolysis with alcoholic potash, the fatty oil gave about 20% of unsaponifiable substance, from which a phytosterol ($C_{26}H_{44}O,H_2O$, m. p. 136°, $[\alpha]_D^{20}$ −31·37°, acetate, m. p. 121°) was isolated. Among the saturated fatty acids, palmitic acid was detected. From the unsaturated acid fraction, an acid, $C_{18}H_{34}O_2$, m. p. 44°, b. p. 208—216°/3 mm., probably *iso*oleic acid, was isolated. From the alcoholic extract (1·25—3·90%), oxalic acid (0·29—0·38% of the material) was isolated and from the water extract (3·67—4·10%) a sugar. K. K.

New Constituent of *Atractylis ovata*, Thunb. S. TAKAGI and G. HONGO (*J. Pharm. Soc. Japan*, 1924, No. 509, 539—551).—By steam distillation of *Atractylis ovata*, Thunb. (*Compositæ*), a light yellow, viscous oil is obtained (d^9 0·985, $[\alpha]_D^9$ + 46·5°, acid value 0, saponification value 16·95). It slightly reddens fuchsin–sulphurous acid solution and reduces Fehling's solution when heated. When subjected to fractional distillation in a vacuum, crystals appear in the distillate (yield: 20% of the oil). The name *atractylon* is given to this substance (colourless plates, m. p. 42°, b. p. 131—132°/4 mm., $[\alpha]_D^{21}$ + 39·65°, d_4^{21} 1·0269 and n_D^{21} 1·52627). Its formula is $C_{14}H_{18}O$, and it can be recrystallised from methyl alcohol. The mother-liquor contains no atractylol, $C_{15}H_{26}O$ (cf. Gadamer and Amenomiya, A., 1903, i, 353). Atractylon is unstable in air, changing into a resin. With vanillin and hydrochloric acid, it gives a cherry-red coloration. The pine-shaving hydrochloric acid reaction gives a violet colour. It does not reduce Fehling's solution. It reacts violently with bromine in acetic acid solution, and contains no methoxyl. No acyl derivative could be obtained. It does not combine with hydroxylamine, phenylhydrazine, or semicarbazide, and could not be reduced with sodium and ethyl or amyl alcohol. From these results, atractylon is concluded to be an ether-like compound. Reduction with hydrogen in acetic acid solution, using platinum black as a catalyst, yielded *hexahydroatractylon*, $C_{14}H_{24}O$, a colourless, stable oil, b. p. 135—136°/4 mm., d_D^{20} 0·9919, $[\alpha]_D^{21}$ −34·36°, n_D^{20} 1·50186. K. K.

Constituents of the Tomato. I. K. YOSHIMURA and K. NISHIDA (*J. Chem. Soc. Japan*, 1924, **45**, 57—65).—From an aqueous extract of 100 kg. of tomato (*Lycopersicum esculentum*, Mill., water content 96·01%), the following compounds were isolated: malic acid, 4·45 g.; citric acid, 4·70 g.; adenine hydrochloride, 1·20 g.; arginine, trace; trigonelline chloroaurate, 1·35 g.; choline chloroaurate 0·20 g. K. K.

Nitrogenous Compounds in Pumpkin and Cucumber. K. YOSHIMURA and K. NISHIDA (*J. Chem. Soc. Japan*, 1924, **45**, 49—57).—The pumpkin contained 82% of water. Analysis of the dried substance gave the following results: protein, 13·23%; fats, 2·47%; crude fibre, 8·95%; soluble non-nitrogenous substance, 68·42%; ash, 6·93%. From the aqueous extract of 16 kg. of pumpkin, free from seeds, the following compounds were isolated: adenine hydrochloride, 0·25 g.; arginine nitrate, 1·68 g.; trigonelline hydrochloride, 0·50 g. On extracting 22 kg. of cucumber (water content 96·15%) with hot water, adenine hydrochloride, 0·27 g., and trigonelline chloroaurate, 0·5 g., were isolated. A trace of arginine was detected. K. K.

Microchemical Detection of Acetaldehyde in Fruits. C. GRIEBEL.—(See ii, 791.)

Methylpentosans in Cereals. G. TESTONI.—(See ii, 790.)

Nitrogenous Compounds in the Oil Cake of *Brassica campestris*, var. *Chinensis*, T. Ito. K. YOSHIMURA and S. FUJISE (*J. Chem. Soc. Japan*, 1924, **45**, 42—49).—The cake contained 10·84% of water. Analysis of the dried material gave the following results: total nitrogen, 6·15%; protein nitrogen, 5·60%; non-protein nitrogen, 0·55%; fats, 13·47%; ash, 11·63%. From an aqueous extract of 40 kg. of the cake the following bases were isolated: adenine hydrochloride, 1·2 g.; arginine copper nitrate, 0·6 g.; choline hydrochloride, 43·3 g.; and betaine hydrochloride, 0·85 g. K. K.

Microchemical Detection of Mustard Oils. A. PIETSCHMANN.—(See ii, 793.)

Nitrogenous Constituents of the Juice of the Alfalfa Plant [Lucerne]. I. Amide and Amino-acid Nitrogen. H. B. VICKERY (*J. Biol. Chem.*, 1924, **60**, 647—655).—The filtrate obtained from the press-juice after raising the alcohol content to 53% (cf. Osborne, Wakeman, and Leavenworth, A., 1922, i, 99, 1104) has been fractionally precipitated with a variety of reagents and the distribution of nitrogen determined in each fraction. Amino-acids are present only in small amount and account for 13·6% of the total nitrogen in the filtrate; small quantities of polypeptides, as shown by the increase in amino-nitrogen after hydrolysis, are also present. Tyrosine and asparagine have been isolated in a pure state; the yield of the latter represented 35·7% of the amide-nitrogen and 5·82% of the total nitrogen in the filtrate. E. S.

Effects of the Method of Desiccation on the Nitrogenous Constituents of Plant-tissue. K. P. LINK and E. R. SCHULZ (*J. Amer. Chem. Soc.*, 1924, **46**, 2044—2050).—Experiments with the leaves of the sugar-beet, the barberry, and maize, and with ears of maize show that the temperature of drying does not affect the total nitrogen content of the tissues but generally produces a decrease in the proportion of total soluble nitrogenous compounds, due to coagulation of the proteins. The effects of desiccation depend largely on the nature of the tissue involved. Drying at high temperatures (80° to 90°) causes a considerable decrease in water-soluble nitrogen, this effect being more pronounced with beet leaves and maize ears than with maize and barberry leaves. At lower temperatures (30° to 45°) proteolytic decomposition takes place, which in some cases is balanced by coagulation of the soluble nitrogenous constituents. At 65° a decrease in the amount of soluble nitrogen is the only significant alteration (cf. Tottingham, Schulz, and Lepkovsky, this vol., i, 598). R. B.

Effect of Titanium on Plant Growth. E. BLANK and F. ALTEN (*J. Landw.*, 1924, **72**, 103—110).—The authors were unable to confirm the results of Němec and Káš (A., 1923, i, 1161) and find that the addition of sodium titanate may depress the dry weight of mustard and maize plants. This depression appears to be directly proportional to the amount of titanate added. O. O.

Have Green Plants the Power of Fixing Elementary Nitrogen from the Atmosphere? C. B. LIPMAN and J. K. TAYLOR (*J. Franklin Inst.*, 1924, **198**, 475—506).—Wheat and barley in culture solutions with and without nitrate nitrogen fix atmospheric nitrogen without bacterial intervention. Incomplete experiments suggest that *Bromus villosus* is able to fix nitrogen, but that peas cannot. Barley does not fix as much elementary nitrogen as wheat in the presence of nitrates in solution. In the case of wheat, there appears to be a minimum supply of nitrate nitrogen below which decrease in the amount of such nitrogen has no effect on the nitrogen content of the dry matter produced. O. O.

Significance of Oxygen for the Formation of Enzymes in Germinating Plant Seeds. A. OPARIN and A. BACH (*Biochem. Z.*, 1924, **148**, 476—481).—The increases in the peroxydase, protease, and amylase contents of moistened wheat seedlings, kept for two days out of contact with oxygen, become more marked if oxygen be admitted. Autolysis of the material in the absence of oxygen causes a diminution in catalase, whilst in the presence of this gas a still greater diminution is noted. On subjecting the seedlings or extracts made from them to anodic oxidation the enzymes first increase to a maximum and then diminish in amount. Peroxydase is present in plant fibrin after tryptic digestion followed by anodic oxidation, but it is not detectable in the original material. A similar treatment of egg-albumin and crystallised plant-globulin yields negative results. J. P.

Can Measurements of Enzyme Action be Employed for Ascertaining the Vitality of Important Cultivated Plants? T. BIÉCHY (*Fermentforsch.*, 1924, **8**, 135—166).—Comparison of the activity of the catalase contained in the expressed juice of the stems of potato plants grown under different conditions shows that this measurement may afford useful evidence regarding the vitality of the plant. It is suggested that this method of investigation be extended to other species. C. R. H.

Resistance to Disease in Plants. J. J. WILLAMAN, C. A. MORROW, and A. K. ANDERSON (*Minnesota Agr. Expt. Sta., Ann. Rept.*, 1922, 35 pp.).—The principal products of metabolism of the flax wilt organism (*Fusarium lini*) are stated to be carbon dioxide and alcohol, with smaller amounts of organic acids.

CHEMICAL ABSTRACTS.

Apparently Specific Test for Tannins. A. H. WARE.—(See ii, 789.)

Influence of Electrolytes on the Total Surface of Soil Particles. L. SMOLIK (*Compt. rend.*, 1924, **179**, 211—213).—The effect of electrolytes on the hygroscopic behaviour of soils has been examined. The addition of an electrolyte apparently coagulates the soil colloids, and thus reduces the surface and the power of absorbing moisture. Removal of the electrolytes by washing has the converse effect. [Cf. *B.*, 1924, 920.] M. S. B.